CALCULATIONS
OF
ANALYTICAL CHEMISTRY

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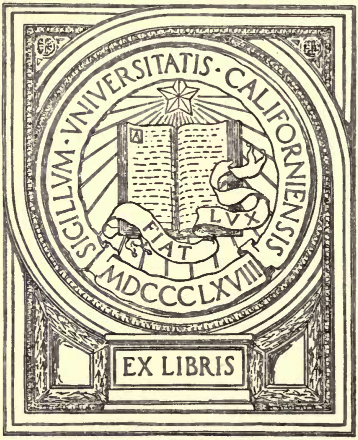

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1900

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ANALYTICAL CHEMISTRY

BY

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IN
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PREFACE.

THIS text-book is intended for use in scientific schools and colleges, in connection with courses in analytical chemistry, and aims to give a logical treatment of the calculations required of an analyst. As analytical chemistry is so closely allied with the other branches of chemistry, many of the calculations given will be found of general application. The matter has been selected so as not to encroach on the domain of physical chemistry but is intended to lead up to the study of that subject.

The object has been to furnish a text-book, which shall give the necessary information concerning those important chemical calculations, which every student should thoroughly understand before taking up advanced work. The method of presentation and arrangement differs materially from the old books on chemical calculations. Formulæ have been avoided, except in the last chapters, so that the student shall consider each problem individually and solve it from a knowledge of chemical laws instead of substituting in formulæ for different cases. If the student has in this way obtained ability to apply the laws, he can readily construct a formula or table for constant use.

More than two hundred examples are given, with answers; all of which can be solved by arithmetic or algebra. They have been made as practical as possible in order to connect chemical laws with practical work. Numerous tables, which have been carefully verified, will be found at the back of the book.

The assistance of Prof. Freedman of the University of Vermont on Chapter X. and of Dr. Joüet in correcting proof and verifying examples is gratefully acknowledged. Any corrections or suggestions will be much appreciated.

E. H. M.

HAVEMEYER HALL,
January, 1900.

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CHAPTER I.

CALCULATION OF CHEMICAL EQUIVALENTS AND ATOMIC WEIGHTS.

CHEMICAL EQUIVALENTS.

THE calculations of analytical chemistry are based on the constant relations existing between the different elements in a chemical compound. These relations are best expressed by equivalents, that is, the weight of the element equivalent to one part of hydrogen. They are the equivalent quantities which will enter into reaction with one part by weight of hydrogen.

For example, if we decompose water by an electric current, we have hydrogen and oxygen given off and for every gram of hydrogen we find eight grams of oxygen, therefore the equivalent of oxygen is eight, for eight parts by weight of oxygen combine with one part by weight of hydrogen to give nine parts of water.

The equivalent of copper may be obtained as follows: When pure black oxide of copper is heated in a stream of hydrogen, the oxide is reduced to metallic copper and the oxygen combines with the hydrogen to form water, which can be absorbed by a weighed calcium chloride tube and reweighed after the experiment.

Suppose we take four grams of black oxide of copper and carry on the experiment until no more water is formed: then weigh; the metallic copper remaining is

3.196 grams: the loss in weight is the oxygen which was combined with the copper; so, as we know the equivalent of oxygen to be 8, if we make the proportion 3.196 (the weight of copper) : 0.804 (the weight of oxygen) : : x : 8, x will be the equivalent of copper, 31.8. Or weigh the water formed (the increased weight of the calcium chloride tube): this is 0.9045 gram. From this we can obtain a direct comparison between hydrogen and copper; for, of the 0.9045 gram of water, 0.8040 gram is the oxygen lost by the copper oxide, so 0.9045–0.8040 or 0.1005 gram is the weight of hydrogen which has combined with the oxygen previously in combination with copper; hence $\frac{3.196}{0.1005}$ or 31.8 is the weight of copper equivalent to one gram of hydrogen or the chemical equivalent of copper.

To obtain the equivalent of bismuth, the metal can be treated with nitric acid until it is completely converted to oxide and after ignition weighed.* 3.6770 grams of bismuth gave 4.1016 grams of oxide. The increased weight 0.4246 gram is the oxygen combined with 3.6770 grams of bismuth, hence the equivalent of bismuth will be found from the proportion

$$3.6770 : 0.4246 : : x : 8. \quad x = 69.27.$$

If we heat finely divided bismuth with an excess of sulphur and add small portions of sulphur until the bismuth is completely converted to sulphide, then remove the excess of sulphur by digesting with a caustic alkali solution, we can from the increased weight find the equivalent of sulphur. For example, 3 grams of bismuth gave 3.6928 grams of sulphide. To get the equivalent of sulphur. $3 : 0.6928 : : 69.27 : x. \quad x = 16.$

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* Schneider, J. präkt. Chem. [2], 50,461.

We have now the following equivalents: Oxygen, 8; Copper, 31.8; Bismuth, 69.27; Sulphur, 16. To obtain that of silver, heat together pure finely divided silver and an excess of sulphur, volatilize the excess of sulphur and weigh the resulting silver sulphide. Suppose these to be the results : 4 grams of silver gave 4.592 grams of sulphide; then $0.592 : 4 :: 16 : x \quad x = 108$, the equivalent of silver. Now that we have obtained the equivalent of silver, we can combine it with a number of elements and get their equivalents. For example, dissolve three grams of silver in nitric acid and pass in chlorine until the silver is completely precipitated or pass chlorine over the silver heated in a combustion tube until it is completely converted into chloride: weigh the silver chloride; weight, 3.9861 grams. To calculate the equivalent of chlorine we have $0.9861 : 3 :: x : 108$. $x = 35.5$. In a similar way the equivalents of bromine and iodine can be found.

This process of obtaining one equivalent from another can be carried on indefinitely until those of all the known elements have been determined, but each successive comparison involves an increase of error so that whenever possible these indirect results are confirmed by a direct comparison with hydrogen or oxygen. In the course of such a set of determinations, it frequently occurs that two or more entirely different equivalents are obtained for the same element.

This shows that the element may combine in different proportions and as the different equivalents are invariably multiples of the lowest, it proves that the elements combine in simple and definite proportions represented by whole numbers.

To illustrate this: suppose in the experiment described with black oxide of copper, we substitute red oxide—4 grams as before, and weigh the copper remaining—3.553 grams. We shall have to obtain the equivalent of copper

$$3.553 :: 0.447 :: x : 8. \quad x = 63.6,$$

which is exactly double that obtained from the black oxide, so that 8 parts by weight of oxygen combine in one case with 31.8 parts of copper and in the other with 63.6 parts. This leads to the conclusion that the red oxide contains exactly one half as much oxygen as the black oxide in proportion to copper. When we attempt to construct formulae from these results, we are confronted by a difficulty, for Cu_2O and CuO or CuO and CuO_2 equally well represent the proportions of oxygen to copper found. To distinguish between these, both molecular weight determinations and study of the salts corresponding to the respective oxides and the analogous compounds of similar elements, are necessary.

Equivalents may also be determined electrolytically, for according to Faraday's Law, the same quantity of electricity precipitates or liberates chemically equivalent quantities of all elements. Suppose we connect in series, cells containing suitable solutions of cuprous copper, cupric copper and of silver respectively, each provided with platinum electrodes; then pass a weak current through the three, as they are connected in series they obtain the same current; so that the weights of metal precipitated are proportional to the chemical equivalents. Suppose the weights precipitated are silver 0.756 gram; copper, 0.4452 in one case, and 0.2226 in the other. If we know one equivalent we can find the others; if we know that of silver to be 108, to find the two equivalents of copper we have

$$0.756 : 0.4452 :: 108 : x. \quad x = 63.6.$$
$$0.756 : 0.2226 :: 108 : y. \quad y = 31.8.$$

For the relations between chemical and electrochemical equivalents see Chapter X.

ATOMIC WEIGHTS.

The atomic weight of an element is the weight of an atom compared with the weight of an atom of hydrogen taken as unity or an atom of oxygen taken as sixteen. This latter definition is very generally adopted, for the ratio of oxygen to hydrogen has been found by most careful experiments to be not 16 to 1 but 15.88 to 1 and, as the value for oxygen enters into a great number of atomic weight calculations, it is more convenient to take it as a whole number, 16, and make it the base of the system. If we use $O = 16$, hydrogen then becomes 1.008 when great exactness is required.

The atomic weight is equal to, or a multiple of, the equivalent, for an element can combine with one or more hydrogen atoms or some other element in different proportions depending on its valence, and while this affects its equivalent it does not its atomic weight which is an invariable property of the element. To determine which multiple of the equivalent is the atomic weight is sometimes a matter of difficulty; which requires a knowledge of the laws and methods of physical chemistry for its certain solution, particularly those regarding molecular weights, which are not within the province of this book. If, however, we take the least common multiple of the equivalents, when the element has several, we get a number which satisfies all analytical data and is the atomic weight subject to confirmation by physical data and the periodic law.

In order not to leave the question of atomic weights in such a vague condition, let us assume the correctness of the following facts, for the proof of which the student is referred to books on physical chemistry.

1. That the product of the specific heat of an element in the solid state and the atomic weight is a constant (approximately) 6.4. Law of Dulong and Petit.

2. That equal volumes of all gases under the same temperature and pressure contain the same number of molecules. Law of Avogadro.

3. That the gaseous molecules of all elements consist of two atoms, except potassium, sodium, zinc, cadmium, and mercury which are monatomic, phosphorus and arsenic which are tetratomic and sulphur which is variable according to temperature. (Phosphorus, arsenic and sulphur are diatomic however at very high temperatures).

With the aid of these facts we can readily confirm our provisional atomic weights as follows:—The least common multiple of our equivalents for copper, 31.8 and 63.6, is 63.6; the specific heat of copper is 0.095 (see table) $63.6 \times 0.095 = 6.042$; a result which approximates 6.4 with sufficient closeness to show any other multiple of the equivalent to be incorrect. Again we found the equivalent of silver to be 108; its specific heat is 0.057 and the product is 6.15, a result which shows that the atomic weight and equivalent of silver are identical.

This principle can be applied to all elements whose specific heats in the solid state are accurately known, but will not aid us to confirm the atomic weight of many of the non-metallic elements. To do this we must consider the other facts. Take a diatomic molecule such as chlorine and compare the weight of a liter of this with the weight of a liter of hydrogen, at the same temperature and pressure. According to the law of Avogadro these volumes contain the same number of molecules. Let x=number of molecules in a liter, then weight x chlorine molecules: weight x hydrogen molecules:: weight one chlorine molecule: weight one hydrogen molecule. And as one chlorine molecule and one hydrogen molecule each contain two atoms, we have, weight liter of chlorine: weight liter of hydrogen:: atomic weight of chlorine: atomic weight of hydrogen: or 3.1673 : 0.0896 : : x : 1. x=35.35. A result which confirms with sufficient accuracy our equivalent 35.5 as the atomic weight of chlorine,

To determine the atomic weight of mercury.

1. Ignite 5 grams of mercuric oxide and weigh the resulting mercury—4.62 grams. The loss in weight 0.38 gram is oxygen and the equivalent of oxygen is 8 so 0.38 : 4.62 : : 8 : x. x = 97.26. The equivalent of mercury.

2. Dissolve 5 grams of corrosive sublimate in water, acidify with nitric acid and precipitate the chlorine in combination by silver nitrate. Weigh the silver chloride, 5.2952 grams. We have found the equivalents of chlorine and silver to be 35.5 and 108, therefore to get the chlorine in this precipitate we have

108 + 35.5 : 35.5 : : 5.2952 : x. x = 1.3099 grams,

the amount of chlorine combined originally with the mercury; 5—1.3099 = 3.6901, the amount of mercury present in the five grams of mercuric chloride. So to get the equivalent of mercury we have,

3.6901 : 1.3099 : : x : 35.5. x = 100.+

3. Fuse 5 grams of calomel with an excess of alkaline carbonate in a porcelain crucible, leach out the alkaline chloride formed and precipitate it with an excess of silver nitrate; weigh the silver chloride, 3.0466 grams.

Calculate the chlorine present as before

$$143.5 : 35.5 :: 3.0466 : x. \quad x = 0.7537 \text{ gram.}$$

To calculate the equivalent of mercury we have

$$5. - 0.7537 : 0.7537 :: x : 35.5. \quad x = 200.$$

We have before us three equivalents of mercury, between the first and second, the indirect determination has the greater probability of accuracy on account of loss of mercury by heating, so the two reliable equivalents are 100 and 200. Therefore the provisional atomic weight, the least common multiple, is 200. This is easily confirmed by the specific heat: 0.0319 times 200 = 6.38. So that 200 is the atomic weight of mercury and we can assign to the two chlorides formulae of $HgCl$ and $HgCl_2$ unless their molecular weights show them to be multiples.

EXAMPLES.

For specific heat of metals see tables on page 162.

1. Five grams of pure zinc were treated with dilute hydrochloric acid and the hydrogen evolved was dried, measured and the corresponding weight calculated; this was 0.1529 gram. What is the equivalent and the atomic weight of zinc? *Ans.* 32.7 and 65.4.

2. One gram of pure metallic magnesium was burned in an atmosphere of oxygen and the resulting oxide collected and weighed. Weight 1.658 grams. What is the atomic weight of magnesium? *Ans.* 24.31.

3. a. Two grams of silver were dissolved in nitric acid and bromine water added until no more precipitate formed. Weight of silver bromide was 3.481 grams. Given the equivalent of silver, 108. What is the equivalent of bromine? *Ans.* 79.97.

b. Given the weight of a liter of bromine vapor, 7.1675 grams and the weight of a liter of hydrogen under the same conditions, 0.0896 gram. What is the atomic weight of bromine? *Ans.* 79.99.

4. Three grams of silver are precipitated by an excess of iodine. Weight of silver iodide was 6.5277 grams.

Three grams of silver are precipitated by an excess of chlorine. Weight of silver chloride, 3.9861 grams.

Given the equivalent of chlorine, 35.5. What is the equivalent of iodine? *Ans.* 127.

5. Roscoe found that 6.4428 grams of Cape diamonds gave 23.6275 grams of carbon dioxide when burned in air.

Van der Plaats found that 30.8891 grams of sugar charcoal gave 113.2320 grams of carbon dioxide. Given O = 16. What is the atomic weight of carbon?

Ans. 12.

6. Richards and Rogers found that 2.35079 grams of zinc bromide gave 3.91941 grams of silver bromide. Given Br = 79.95 and Ag = 107.92. What are the equivalent and atomic weights of zinc?

Ans. 32.73 and 65.46.

7. Winkler converted electrolytically deposited nickel to a dry chloride and then weighed the chlorine as silver chloride. He obtained from 0.3011 gram of nickel 1.4621 grams of silver chloride. Given Ag = 107.92 and Cl = 35.37. What are the equivalent and atomic weights of nickel? *Ans.* 29.5 and 59.

8. Deville found that 0.6763 gram of boron chloride, obtained by the action of gaseous hydrochloric acid on boron, gave 2.4770 grams of silver chloride. Given Ag = 107.92 and Cl = 35.37. What is the chemical equivalent of boron? *Ans.* 3.75.

9. Dumas found that it required 4.168 grams of silver (as nitrate) to precipitate the chlorine from 4.0162 grams of anhydrous barium chloride. Given the equivalents of silver and chlorine, 107.92 and 35.37. What is the chemical equivalent of barium? *Ans.* 68.62.

10. Stas found that after adding 7.25682 grams of potassium chloride to 10.51995 grams of silver, dissolved in nitric acid, that 0.0194 gram of silver remained in solution. Given the atomic weights of chlorine and silver as 35.37 and 107.92. Calculate that of potassium.

Ans. 39.2.

11. Mallet determined the atomic weight of aluminium by the following methods:

(a) by oxidizing to water the hydrogen evolved when aluminium was dissolved by sodium hydroxide: 5.2632 grams of aluminium gave 5.2562 grams of water.

(b) by precipitating the bromine in aluminium bromide as silver bromide: 8.6492 grams of aluminium bromide required 10.4897 grams of silver.

Calculate the atomic weight of aluminium. Given Ag = 107.92, Br = 79.95, O = 16, H = 1.008.

Ans. (a)27.06. (b)27.105.

12. If 5 grams of a metallic bromide gave 7.2552 grams of iodide, and the atomic weights of bromine and iodine are 79.95 and 126.85 respectively. What would be the atomic weight of the metal if it were univalent, bivalent or trivalent? *Ans.* 24, 48, 72.

After this introduction on the determination of atomic weights, the student should have a definite idea of their meaning and how they can be obtained. In the calculations and examples from this point the atomic weights given on page 159 will be used unless especially mentioned. These were adopted by the American Chemical Society and published in the Journal for February, 1899.

CHAPTER II.

CALCULATION OF FORMULAE AND PERCENTAGE.

FORMULA FROM PERCENTAGE.

In any chemical compound, if we divide the percentages obtained from analysis by the atomic weights of the elements, we shall get numbers which represent the ratio of atoms, and on reducing these to the nearest whole numbers, obtain the empirical formula—the simplest ratio of atoms. The correct formula may however be a multiple of this which would have the same percentage composition. Therefore a determination of the molecular weight is necessary to decide what multiple of the empirical formula is the correct one. For the methods and calculations used in determining molecular weights, except from the specific gravity of a gas, the reader is referred to the numerous text books on physical chemistry.

The empirical formula is usually obtained from an analysis, and while the proper multiple should be used in all equations, yet the empirical formula serves many useful purposes in inorganic analysis, such as furnishing data for normal solutions, factors, etc., just as correctly as the proper molecular formula.

In organic chemistry, this is not the case as the existence of many totally different bodies having the same empirical formula, makes it essential to use the molecular or better the graphic formulae. The following examples illustrate the calculation of empirical formulae:

A salt gave on analysis 52.45% of potassium and 47.55% of chlorine,

$$\begin{array}{l} 52.45 \div 39.11 = 1.341, \\ 47.55 \div 35.45 = 1.341, \end{array}$$

the ratio of atoms is 1.341 to 1.341 or 1 to 1, so the formula has an equal number of atoms of potassium and chlorine and the empirical formula is KCl.

A salt gave on analysis the following:

$$\left.\begin{array}{llll} \text{Phosphorus} & - & 21.82\% \div 31.02 & = 0.703 \\ \text{Hydrogen} & - & 0.71\% \div 1.01 & = 0.703 \\ \text{Sodium} & - & 32.43\% \div 23.05 & = 1.407 \\ \text{Oxygen by difference} & & 45.02\% \div 16. & = 2.814 \end{array}\right\} \begin{array}{c} \text{Ratio} \\ \text{of} \\ \text{Atoms.} \end{array}$$

If we divide the numbers representing the ratio of atoms by the greatest common-divisor 0.703 we get the ratio expressed in the nearest whole numbers, or phosphorus 1; hydrogen 1; sodium 2; oxygen 4. The empirical formula is therefore $PHNa_2O_4$ or as it is usually written Na_2HPO_4.

Analysis of ignited magnesium ammonium phosphate gave the following results:

$$\begin{array}{llll} \text{Magnesium} & 21.82\% \div 24.29 & = 0.898 \div 0.449 & = 2. \\ \text{Phosphorus} & 27.86\% \div 31.02 & = 0.898 \div 0.449 & = 2. \\ \text{Oxygen} & 50.32\% \div 16. & = 3.145 \div 0.449 & = 7. \end{array}$$

The greatest common divisor of the numbers representing the ratio of atoms is 0.449: dividing by this we obtain the nearest whole numbers. So the empirical formula is $Mg_2P_2O_7$.

FORMULAE OF MINERALS.

From the results of analysis the formula of a mineral can be calculated as in the case of any other empirical formula; but as one element or group often replaces another to a greater or less extent without altering the mineralogical character, those elements which may replace each other are grouped together and represented by the letter R. So oxides of the monatomic elements, such as the alkalies, are represented by R_2O; oxides of the diatomic elements, such as calcium, magnesium, barium, ferrous iron, manganese, etc., by RO; oxides of aluminium, chromium, ferric iron, manganic manganese, etc., by R_2O_3 and so on. In this way the composition of the mineral is indicated and especially the ratio of basic to acid oxides.

For example, analysis of Franklinite gave the following results:*

	(1)	(2)	(3)
Fe_2O_3	60.52	66.34	67.42
Mn_2O_3	6.79	——	——
ZnO	19.44	20.26	6.78
MnO	12.81	12.31	9.53
FeO	——	——	15.65

We see in (1) a replacement of part of the Fe_2O_3 by Mn_2O_3; so that R_2O_3 in this case is ferric iron and manganic manganese, comparing (1), (2), and (3), we see that the percentages of ZnO, MnO and FeO vary greatly, these constitute the RO group.

In (1) calculate from the percentage of Mn_2O_3 the equivalent percentage of Fe_2O_3. To do this we have, the percentage of Mn_2O_3 is to the percentage of Fe_2O_3 as the molecular weight of Mn_2O_3 is to the molecular weight of Fe_2O_3. The molecular weight of Mn_2O_3 is $(2 \times 55) + † (3 \times 16)$ or 158 and that of Fe_2O_3 is $(2 \times 56) + (3 \times 16)$ or 160. So the proportion becomes,

$$6.79 : x :: 158 : 160. \quad x = 6.88\%.$$

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* Dana's Mineralogy.

† In these calculations the atomic weights to one decimal place are sufficient.

In the same way, using the proper molecular weights, calculate the percentage of MnO, to the equivalent percentage of ZnO,

$$12.81 : y :: 71. : 81.4. \quad y = 14.68\%.$$

We have now Fe_2O_3, $60.52\% + 6.88\% = 67.40\%$ and ZnO, $19.44\% + 14.68\% = 34.12\%$. Dividing these by the molecular weights we get

$$\begin{aligned} 67.40\% \div 160 &= 0.421 \div 0.420 = 1.+ \\ 34.12\% \div 81.4 &= 0.419 \div 0.420 = 1.- \end{aligned}$$

These results are almost identical, so the ratio of R_2O_3 to RO is 1 to 1 and the formula is represented by RO,R_2O_3.

There was no particular reason for calculating the percentage of MnO to ZnO rather than ZnO to MnO; the result when divided by the proper molecular weight will be the same in either case.

The typical formula can also be found by dividing the percentage of each oxide by its molecular weight and then grouping together the ratios as follows—

$$\text{(2)}\quad Fe_2O_3\ 66.34 \div 160 = 0.414.$$

$$\left.\begin{aligned} \text{ZnO}\quad 20.26 \div 81.4 &= 0.249 \\ \text{MnO}\quad 12.31 \div 71. &= 0.172 \end{aligned}\right\} = 0.421.$$

The ratio is approximately one to one as before. The lack of agreement in the figures representing the ratio is probably due to a deficiency in the percentage of R_2O_3 elements for the percentages only add up to 98.91.

From the third analysis we get 0.421 : 0.435, again showing the ratio to be one to one.

So from the results of these three analyses we find the formula of Franklinite to be (Zn Mn Fe)O, $(Fe\ Mn)_2O_3$.

Dana's Mineralogy gives the following analyses of garnets,

	(1)	(2)
SiO_2	40.90	39.85
Al_2O_3	22.81	22.07
Fe_2O_3	——	1.13
Cr_2O_3	1.48	——
FeO	13.34	——
MnO	0.38	——
MgO	16.43	0.68
CaO	4.70	36.31

The R_2O_3 bases are calculated to Al_2O_3 as the percentages of Fe_2O_3 and Cr_2O_3 are small and indicate a partial replacement of the Al_2O_3. With the RO bases we may calculate either to CaO or MgO and divide the sum of the resulting percentages by the molecular weight of the oxide we select. After calculating Cr_2O_3 and Fe_2O_3 to Al_2O_3 and FeO, MnO, and MgO to CaO we get

(1)

SiO_2	$40.90\% \div 60.4 = 0.677.$	3.
$Al_2O_3(R_2O_3)$	$23.80\% \div 102.2 = 0.236.$	1.
CaO (RO)	$38.37\% \div 56. = 0.685.$	3.

(2)

SiO_2	$39.85\% \div 60.4 = 0.660.$	3.
$Al_2O_3(R_2O_3)$	$22.79\% \div 102.2 = 0.223.$	1.
CaO (RO)	$37.26\% \div 56. = 0.665.$	3.

So in both cases the type formula is $3RO, R_2O_3, 3SiO_2$.

In connection with silicates both natural and artificial (slags) the term "oxygen ratio" is often used. This means the ratio of the oxygen atoms belonging to the basic groups to those combined with silicon. In the garnet we have six oxygen atoms combined as basic oxides and six as an acid oxide (SiO_2), hence the oxygen ratio is one to one, or if it is desired to distinguish between the basic oxides 1 : 1 : 2. In writing these ratios the order adopted is first RO, then R_2O_3 and last SiO_2.

PERCENTAGE COMPOSITION FROM FORMULA.

If we have the formula of a compound whether molecular or empirical and the atomic weights of its elements the calculation of the percentage composition is made as follows.—Take for example sodium chloride; we have the formula NaCl and the atomic weights Na 23.05 and Cl 35.45. The molecular weight is the sum of the atomic weights, $23.05 + 35.45 = 58.5$, the molecular weight of NaCl. Let $x = \%$ Na and $y = \%$ Cl then

$$23.05 : 58.5 :: x : 100. \quad x = 39.402\%.$$
$$35.45 : 58.5 :: y : 100. \quad \underline{y = 60.598\%}.$$
$$\text{To prove } x + y = 100.00\%.$$

To calculate the percentage composition of ethyl alcohol, C_2H_5OH. The molecular weight is $24.00 + 6.05 + 16 = 46.05$. Let $x = \%C$, $y = \%H$ and $z = \%O$.

$$24. : 46.05 :: x : 100. \quad x = 52.117\% \text{ C}.$$
$$6.05 : 46.05 :: y : 100. \quad y = 13.138\% \text{ H}.$$
$$16. : 46.05 :: z : 100. \quad \underline{z = 34.745\% \text{ O}}.$$
$$\text{To prove } x + y + z = 100\%.$$

By similar proportions the percentage composition of any substance whose formula is known can be calculated.

CALCULATION OF PERCENTAGE TO THE DRY BASIS.

Ores and other material often contain moisture: it is frequently necessary to calculate what the percentage of a constituent would be if this water were removed and the reverse.

If an ore contains 10% of moisture and 42% of manganese, what will be the percentage of manganese on the dry basis? Let us represent the weight of the wet sample by 100 parts; then after drying we will have 100—10 (the parts of water): let x = the percentage of manganese on the dry basis; then, as no manganese is lost or gained by the removal of water, we have $42 \times 100 = x (100-10)$. $x = 46.66\%$ or, in general if we divide the percentage by 100 minus the percentage of moisture we get the percentage on the dry basis.

If an ore contains 58% of iron on the dry basis, what is the percentage of iron when 18% of water is present?

$$58 : x :: 100 : 82. \quad x = 47.56$$

for the original ore may be regarded as made up of 82 parts of dry ore containing 58% of iron and 18 parts of water containing no iron.

EXAMPLES.

Calculate the empirical formulae from the following analytical results.

1. Lead 68.30%. Sulphur 10.55%. Oxygen by difference, 21.15%. *Ans.* $PbSO_4$.

2. Arsenic 41.32%. Chlorine 58.66%. *Ans.* $AsCl_3$.

3. Potassium 35.56%. Iron 17.00%. Cyanogen by difference, 47.44%. *Ans.* $K_3Fe\ C_6N_6$.

4. Carbon 37.5%. Hydrogen 12.5%. Oxygen by difference, 50.%. *Ans.* CH_4O.

5. Carbon 40.67%. Hydrogen 8.47%. Nitrogen 23.73%. Oxygen by difference, 27.13%. *Ans.* C_2H_5NO.

6. Carbon 46.75%. Hydrogen 6.48%. Nitrogen 36.36%. Oxygen by difference, 10.41%. *Ans.* $C_6H_{10}N_4O$.

Calculate the formulae of the following minerals.

7. Pyrargyrite. (*) Sulphur 17.81%. Antimony 22.45%. Silver 59.75%. *Ans.* Ag_3SbS_3.

8. Enargite. Sulphur 32.69%. Arsenic 19.47%. Copper 47.84%. *Ans.* Cu_3AsS_4.

9. Bournonite. Sulphur 19.36%. Antimony 23.57%. Arsenic 0.47%. Lead 41.95%. Copper 13.27%. Iron 0.68%. *Ans.* $(PbCu_2)_3Sb_2S_6$.

10. Atacamite. Chlorine 16.45%. Copper 14.72%. Copper oxide (CuO) 55.26%. Water 13.57%. *Ans.* $Cu_2Cl\ H_3O_3$.

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* These percentages are taken from Dana's Mineralogy.

11. Barytocalcite. Carbonic acid 29.44%. Barium oxide 50.36%. Calcium oxide 19.22%. Manganous oxide 0.25%. *Ans.* $BaCO_3$,$CaCO_3$ or RCO_3.

12. Given the following analysis of augite: SiO_2 54.28%, Al_2O_3 0.51%, Fe_2O_3 0.98%, FeO 1.91%, MgO 17.30%, CaO 25.04%. Calculate its formula and oxygen ratio. *Ans.* $CaMgSi_2O_6$ and 1 : 2.

13. Find the type formula and oxygen ratio for a mineral whose composition is SiO_2 38.03%, Al_2O_3 20.83%, FeO 36.15%, MnO 2.14%, MgO 0.97%, CaO 2.73%. *Ans.* 3RO, R_2O_3, $3SiO_2$ and 1 : 1.

14. The mineral Zirkelite on analysis yielded the following results: ZrO_2 52.89%, TiO_2 14.95%, ThO_2 7.31%, Ce_2O_3 2.52%, (Y_2O_3)? 0.21%, $UO_2$1.40%, FeO 7.72%, CaO 10.79%, MgO 0.22%, loss on ignition 1.02%. What is the formula? (*)

Ans. RO.2,(Zr, Ti, Th,)O_2,.

Calculate the percentage composition of the following compounds.

15. Potassium Sulphate, K_2SO_4.

Ans. K, 44.88%. S, 18.40%. O, 36.72%.

16. Manganous Sulphate, $MnSO_4$.

Ans. Mn, 36.42%. S, 21.23%. O, 42.36%.

17. Lithium Phosphate, $Li_3(PO_4)_2$.

Ans. Li, 9.99%. P, 29.38%. O, 60.62%.

18. Zinc pyrophosphate $Zn_2P_2O_7$.

Ans. Zn, 42.91%. P, 20.35%. O, 36.72%.

19. Urea, CH_4N_2O and Ammonium Cyanate, NH_4CNO.

Ans. C, 19.96%. H, 6.71%. N, 46.71%. O, 26.61%.

20. Benzyl Chloride $C_6H_5CH_2Cl$.

Ans. C, 66.40%. H, 5.58%. Cl, 28.02%.

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* Mineralogical Magazine 1895-97. XI, 180.

21. Nitrotoluene $C_6H_4(NO_2)\,CH_3$.

Ans. C, 61.27%. H, 5.14%. N, 10.24%. O, 23.34%.

22. Indigo $C_{16}H_{10}N_2O_2$.

Ans. C, 73.24%. H, 3.84%. N, 10.71%. O, 12.20%.

23. Potassium ferrocyanide, crystallized, $K_4Fe(CN)_6, 3H_2O$. *Ans.* K, 37.00%. Fe, 13.25%. C, 17.03%. N, 19.92%. H, 1.43%. O, 11.35%.

24. A sample of ore contained 20% of lead, 14% of zinc and 14% of water. What are the percentages of lead and zinc on the dry basis.

Ans. Lead 23.25%, Zinc 16.28%.

25. A clay was partially dried and then contained SiO_2 50%, H_2O 7%; the original sample contained 12% of water. What is the percentage of SiO_2 in the original sample. *Ans.* 47.37%.

CHAPTER III.

CALCULATIONS OF MIXTURES HAVING A COMMON CONSTITUENT.

To calculate the weights of chlorine and bromine in a mixture of silver chloride and bromide.

If we have a solution containing chlorides and bromides and wish to determine the weights of chlorine and bromine present, we can precipitate these elements by silver nitrate and weigh the resulting mixture of AgCl and AgBr, weight 1.50 grams. Then by scorification or some other method, determine the silver; weight 1.00 gram. We have the atomic weights of silver 107.92, chlorine 35.45, bromine 79.95, the weight of the mixture and the weight of the common constituent, silver.

If all the silver were present as chloride the weight would be 1.32848 grams: for as we know the formula and atomic weights we have the proportion

107.92 : 143.37 :: 1. : x.

At. wt. Ag : Mol. wt. AgCl : : wt. Ag : wt. AgCl, which gives x = 1.32848, the weight of silver chloride corresponding to the silver found. But we have 1.50 grams of mixed chloride and bromide, hence 1.50-1.32848 or 0.17152 gram is the excess in weight due to the greater atomic weight of bromine and therefore proportional to the weight of bromine present. So to obtain the weight of bromine we have :

79.95 − 35.45 : 79.95 :: 0.1715 : x.

At. wt. Br - At. wt. Cl : At. wt. Br : : excess in wt. : wt. Br.

$x = 0.30815$, weight Br. The weight of chlorine will be:

Weight silver, chlorine and bromine	1.50000 grams
weight silver (1.) and bromine (0.30815)	1.30815 grams
or	0.19185 gram

To calculate the chlorine directly: find the weight of silver bromide corresponding to the silver present.

$$107.92 : 187.87 :: 1 : x. \quad x = 1.74082 \text{ grams.}$$

But we have only 1.5 grams of the mixture so 1.74082 - 1.5 or 0.24082 is the deficiency due to the lower atomic weight of chlorine and proportional to the weight of chlorine present.

Let $y =$ weight of chlorine, then we have

$$79.95 - 35.45 : 35.45 :: 0.2408 : x$$

and $x = 0.19183$ the weight of chlorine present, which confirms the result obtained by difference.

It would be more logical to say that the excess in weight is due to the greater molecular weight of AgBr or the deficiency due to the lower molecular weight of AgCl, but this only means the addition of 107.92 in both cases which does not affect the result after subtraction.

Perhaps the following method is more easily comprehended from a mathematical standpoint but it is longer and the use of logarithms is recommended.

Let $x =$ weight of AgCl and $y =$ weight of AgBr then

$\frac{107.92}{143.37}x =$ weight of silver in AgCl and

$\frac{107.92}{187.87}y =$ weight of silver in AgBr; so, using the same weights as before we have the two equations,

(1) $x + y = 1.50$ and

(2) $\frac{107.92}{143.37}x + \frac{107.92}{187.87}y = 1.$

reducing to decimals we have $0.75274\,x + 0.57444\,y = 1$ substituting for x its value in terms of y from equation, (1) we have

$$0.75274\,(1.5 - y) + 0.57444 = 1 \quad \text{Solving}$$
$$0.1291 = 0.1783\,y. \quad y = 0.7241, \text{ wt. AgBr.}$$

substituting this value in equation (1) we get $x = 0.7759$ wt. AgCl; from which by the following proportions,

$$143.37 : 35.45 :: 0.7759 : \text{wt. Cl and}$$
$$187.87 : 79.95 :: 0.7241 : \text{wt. Br;}$$

we get wt. Br 0.3081 and wt. Cl 0.1918 gram.

Suppose we have the weight of a mixture of potassium and sodium sulphates, 0.3710 gram, and the weight of SO_3, 0.200 gram; to calculate the weights of K_2O and Na_2O. Calculate the SO_3 all to Na_2SO_4,

$$80.07 : 142.17 :: 0.2 : x. \quad x = 0.3551.$$

but as we have 0.3710 gram of mixed sulphates, the excess in weight 0.0159 gram is due to the excess in molecular weight of K_2O over Na_2O and is therefore proportional to the weight of K_2O, so we have the proportion,

$$32.12 : 94.22 :: 0.0159 : x. \quad x = 0.0466$$

K_2O 0.0466 gram. $K_2O. + Na_2O + SO_3 = 0.3710$ gram,
SO_3 0.2000 gram. $K_2O. + SO_3 = 0.2466$ gram
0.2466 gram. $Na_2O = 0.1244$ gram

To solve this example by the other method, let x = weight of K_2SO_4 and y = weight of Na_2SO_4, then $x + y = 0.371$.

The molecular weight of SO_3 is 80.07 and that of K_2SO_4 is 174.29; therefore

$\frac{80.07}{174.29}\,x$ represents the weight of SO_3 present as K_2SO_4

and similarly $\frac{80.07}{142.17}$ y the weight of SO_3 present as Na_2SO_4, so we have for a second equation,
$\frac{80.07}{174.29} x + \frac{80.07}{142.17} y = 0.2$ or after multiplying and removing unnecessary fractions,

$$11383.5\ x + 13955.4\ y = 4955.7$$

substituting from first equation $x = 0.371 - y$ we have
$11383.5\ (0.371 - y) + 13955.4\ y = 4955.7$ or
$2571.9\ y = 732.4.\ y = 0.2847$, weight of Na_2SO_4;
and as $x + y = 0.3710.\ x = 0.0863$, weight K_2SO_4. From which the following proportions will give the weights of K_2O and Na_2O

$94.2 : 174.29 :: \text{wt. } K_2O : 0.0863.\ \text{wt. } K_2O = 0.0466.$
$62.1 : 142.17 :: \text{wt. } Na_2O : 0.2847.\ \text{wt. } Na_2O = 0.1243.$

The following is a more practical example. One gram of commercial sodium bicarbonate gave CO_2, 0.5097 gram and Na_2O, 0.3681 gram. Calculate the weights of $NaHCO_3$ and Na_2CO_3. Let x be the weight of Na_2CO_3 and y the weight $NaHCO_3$; then,

(1) $\frac{44.01}{106.11} x + \frac{44.01}{84.07} y = 0.5097$ and

(2) $\frac{62.1}{106.11} x + \frac{62.1}{168.14} y = 0.3681$

The molecular weight of $NaHCO_3$ is doubled in the second equation as it takes two molecules to give one Na_2O. Reduce the fractional coefficients to the nearest decimals,

(1) $0.4147\ x + 0.5236\ y = 0.5097$

(2) $0.5852\ x + 0.3693\ y = 0.3681$

substituting for x in the second equation its value in terms of y we get

$$0.5852\ \frac{(0.5097-0.5236\ y)}{0.4147} + 0.3693\ y = 0.3681$$

$$0.7192 - 0.7388\ y + 0.3693\ y = 0.3681$$

$0.3695\ y = 0.3511$. $y = 0.9502$, weight of $NaHCO_3$.

Substituting for y in equation (1) 0.9502 we get $0.4147\ x + 0.5236\ (0.9502) = 0.5097$ which gives $x = 0.0294$, weight of Na_2CO_3.

This problem may also be done as follows: Calculate all the CO_2 to $NaHCO_3$, according to the proportion.

$$44.01 : 84.07 : : 0.5097 : \text{wt. } NaHCO_3 :$$

this gives 0.9736 gram; next calculate the weight of Na_2O necessary to combine with this to form the 0.9736 gram of $NaHCO_3$. This is 0.35955 gram, but we have present 0.3681 gram, which leaves an excess of 0.00855 gram. This must be employed to make as many $NaHCO_3$ molecules into Na_2CO_3 molecules as possible and, as one Na_2O furnishes the sodium oxide necessary to convert $2NaHCO_3$ into $2Na_2CO_3$, to find the amount of Na_2CO_3 required by the excess of Na_2O we have:—

$$\begin{array}{ccccc} 62.1 & : & 212.22 & : : & \\ \text{Mol. wt. } Na_2O & : & 2\ (\text{Mol. wt. } Na_2CO_3) & : : & \\ & & 0.00855 & : & x \\ & & \text{wt. } Na_2O \text{ in excess} & : & \text{wt. } Na_2CO_3 \end{array}$$

$x = 0.0292$, weight Na_2CO_3.

The weight of Na_2O present as Na_2CO_3 is twice the excess found or 0.0171 gram. The rest of the Na_2O, $0.3681 - 0.0171$ or 0.3510 gram is present as $NaHCO_3$. To find this weight:—

$0.3510 : x : : 62.1 : 168.12$. $x = 0.9504$, weight of $NaHCO_3$.

These examples show the results to be the same by either method, the figures should be carried out to four decimals or at least three significant figures so that no appreciable error in calculation shall be added to the unavoidable errors of analysis.

FORMATION OF MIXTURES OF DEFINITE COMPOSITION.

Suppose we wish to form 100 lbs. of a mixture containing 10% of calcium carbonate and we have at our disposal lots containing 7% and 23% respectively. How many pounds of each must be taken?

One lot contains 3% less than the desired mixture, the other 13% more, so if we take 3 parts of the richer to 13 of the poorer we shall have a mixture containing 10%.

$$3 : 16 :: x : 100. \quad x = 18.75 \text{ lbs. } (23\%).$$
$$13 : 16 :: y : 100. \quad y = 81.25 \text{ lbs. } (7\%).$$

When the proportions cannot be seen by inspection the following method can be used:

Given two iron ores, one containing 0.42% of phosphorus and the other 0.17%. How much of each must be mixed to give ten tons containing 0.20% of phosphorus? Let x be the weight in tons of the 0.42% ore and 10 — x the weight of the 0.17% ore; then,

$$x\ (0.0042) + (10 - x)\ 0.0017 = 10\ (0.002).$$

This equation is based on the equality in weight of phosphorus in the sum of the two portions, and in the mixture.

Solving, we get $x = 1.2$ tons, $10 - x = 8.8$ tons.

Given waste mixed acid from nitrating whose composition is H_2SO_4 62.178%, HNO_3 19.066%, H_2O 18.756%; sulphuric acid containing 97% H_2SO_4; nitric acid containing 87% HNO_3. What weights of each must be taken to give 1000 lbs. of a mixture containing 61% H_2SO_4, 22% HNO_3 and 17% H_2O without adding water?

Let x be the weight of waste acid,
y " " " sulphuric acid,
z " " " nitric acid,

then x (0.6218) is the weight of H_2SO_4 in the waste acid, y (0.97) the weight of H_2SO_4 in the sulphuric acid, z (0.13) the weight of water in the nitric acid and so on. 1000 lbs. of the desired mixture must contain 610 lbs. H_2SO_4, 220 lbs. HNO_3 and 170 lbs. of water. We have therefore the following equations based on equality of weight:

$$(1)\ x\ (0.6218) + y\ (0.97) = 610.$$
$$(2)\ x\ (0.19066) + z\ (0.87) = 220.$$
$$(3)\ x\ (0.18756) + y\ (0.03) + z\ (0.13) = 170.$$

$$y = \frac{610 - x\ (0.6218)}{0.97} = 628.8 - x\ (0.641)$$

$$z = \frac{220 - x\ (0.19066)}{0.87} = 252.7 - x\ (0.2191)$$

substituting in equation (3)

$$0.18756\ x + 18.864 - 0.01923\ x + 32.851 - 0.02848\ x = 170.$$

$$0.13985\ x = 118.285. \quad x = 845.68.$$

substituting in equation (1)

$$y = \frac{610 - (845.68 \times 0.6218).}{0.97} \quad y = 86.77.$$

substituting in equation (2)

$$z = \frac{220 - (845.68 \times 0.19066).}{0.87} \quad z = 67.54.$$

Proof $845.68 + 86.77 + 67.54 = 999.99.$

EXAMPLES.

1. Given a mixture of KCl and NaCl: weight 1.3306 grams; and weight of chlorine 0.709 gram. What are the weights of K and Na?

Ans. K 0.3911 gram. Na, 0.2305 gram.

2. Given a mixture of $PbSO_4$ and $BaSO_4$; weight 4 grams; and weight of SO_4 1.62 grams. What are the weights of $PbSO_4$ and $BaSO_4$?

Ans. $PbSO_4$ 0.2729 gram. $BaSO_4$ 3.7271 grams.

3. Given a mixture of $HgCl_2$ and HgCl weight 2.35 grams and chlorine 0.45 gram. What is the weight of each chloride?

Ans. HgCl 1.4847 grams. $HgCl_2$ 0 8653 gram.

4. Given a mixture of AgI and AgBr; weight 4.22 grams and weight of silver 2.11 grams. What are the weights of iodine and bromine?

Ans. Iodine 1.4790 grams. Bromine 0.6309 gram.

5. Given a mixture of $NaHSO_4$ and $KHSO_4$: weight 0.5 gram and weight SO_4 0.395 gram. What are the weights of K and Na?

Ans. K 0.0148 gram. Na 0.0860 gram.

6. Given a mixture of K_2CO_3 and $KHCO_3$; weight 1 gram and weight CO_2 0.40 gram. What is the weight of each carbonate?

Ans. K_2CO_3 0.3259 gram. $KHCO_3$ 0.6741 gram.

7. Given a mixture of $K_2C_4H_4O_6$ and $KHC_4H_4O_6$: weight 1 gram and weight of K 0.30 gram. What is the weight of each tartrate?

Ans. $K_2C_4H_4O_6$ 0.6683 gram. $KHC_4H_4O_6$ 0.3316 gram.

8. Given a sample of pure dolomite, $MgCO_3$ and $CaCO_3$: weight 1 gram and CO_2 weight 0.48 gram. Find the weights of CaO and MgO.

Ans. CaO 0.2862 gram. MgO 0.2338 gram.

9. Given a mixture of $CaH_4(PO_4)_2$ and $Ca_3(PO_4)_2$: weight 1 gram and PO_4 weight 0.70 gram. Calculate the weight of each phosphate.

Ans. $\begin{cases} CaH_4(PO_4)_2 \text{ 0.4395 gram.} \\ Ca_3(PO_4)_2 \text{ 0.5605 gram.} \end{cases}$

10. Given a sample of commercial potassium bicarbonate containing 0.4679 gram of K_2O and 0.4338 gram of CO_2 in one gram. How much $KHCO_3$ and K_2CO_3 is there present?

Ans. $KHCO_3$ 0.98 gram. K_2CO_3 0.01 gram.

11. One gram of manganese ore gave on analysis, manganese 0.25 gram and available oxygen 0.05 gram. How much Mn_2O_3 and MnO_2 is there present? By available oxygen is meant the amount over that necessary to form MnO.

Let x = wt. Mn_2O_3 and y = wt. MnO_2 then we have

$$\frac{109\ 98}{157.98}x + \frac{54.99}{86.99}y = 0.25. \qquad \textit{Ans.}\ Mn_2O_3\ 0.2245.$$

$$\frac{16}{157.98}x + \frac{16}{86.99}y = 0.05. \qquad MnO_2\ \ 0.1482.$$

12. Given a sample of argol (crude potassium bitartrate); one gram of which gave 0.2336 gram of K_2O and 0 7310 gram $H_2C_4H_4O_6$. Supposing that there is no other tartrate or potassium salt present, how much $KHC_4H_4O_6$ and $K_2C_4H_4O_6$ is there?

Let x = wt. $K_2C_4H_4O_6$ and y = $KHC_4H_4O_6$, then we have

$$\frac{94.22}{226.29}x + \frac{47.11}{188.19}y = 0.2336 \text{ and } \frac{150.09}{226.29}x + \frac{150.09}{188.19}$$

$y = 0.731$ *Ans.* $\begin{cases} 0.8977 \text{ gram } KHC_4H_4O_6 \\ 0.02 \text{ gram } K_2C_4H_4O_6 \end{cases}$

13. Given manganese ores containing 47% and 23% of manganese respectively. How many pounds of each must be mixed to give a ton containing 39% of manganese. *Ans.* $\begin{cases} 666.67 \text{ lbs. } 23\% \text{ ore.} \\ 1333.33 \text{ lbs. } 47\% \text{ ore.} \end{cases}$

14. Suppose we have ten tons of coal containing 3.5% of sulphur. We have also supplies of coal containing 1.1% and 1.6% of sulphur. How much of each shall we add to the ten tons to make 20 tons containing 2.5% of sulphur? *Ans.* 2 tons 1.1% and 8 tons 1.6%.

15. Given iron ores containing 54% of iron with 0.60% of phosphorus and 47% of iron with 0.20% of phosphorus. What is the percentage of iron in a mixture of these containing 0.28% of phosphorus? *Ans.* 48.4%.

16. Given two alloys: a brass containing copper 65%, zinc 35% and a German silver containing copper 56%, zinc 24%, nickel 20%. What is the composition of the alloy formed by melting these together in such proportion that it contains zinc 30%? (Supposing that there is no loss by oxidation or volatilization during fusion).

Ans. Copper 60.90%, zinc 30%, nickel 9.09%.

17. Suppose we wish to form 100 lbs. of an alloy containing copper 70%, zinc 20%, and tin 10% and we have besides pure copper, a brass, copper ⅔, zinc ⅓ and solder, zinc ½, tin ½. How much of each must be taken?

Ans. Solder 20 lbs., brass 30 lbs., copper 50 lbs.

18. Given pure silver and an alloy containing 890 parts of silver and 110 parts of copper. How many ounces of each must be taken to form 1000 ounces of an alloy, 925 parts of silver and 75 parts of copper?

Ans. 681.8 ozs. of alloy, 318.2 ozs. of silver.

CHAPTER IV.

CALCULATIONS FROM EQUATIONS.

Chemical reactions are best represented by equations; these are the expression of definite and exact quantitative changes and therefore are the basis of most analytical calculations.

Take for example the simple reaction

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl,$$

from a qualitative standpoint this means that, when barium chloride is added to sulphuric acid or the reverse, barium sulphate and hydrochloric acid are formed. This is not all that is shown by the reaction. It shows that one molecule of barium chloride acting on one molecule of sulphuric acid forms one molecule of barium sulphate and two molecules of hydrochloric acid. Now as the relative weights of the different atoms composing the molecules are known, based on oxygen = 16, we can by adding these together get the relative weights of the molecules; so the reaction becomes,

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl.$$

$137.43 + 2(35.45) + 2 + 32.07 + 64 =$

$137.43 + 32.07 + 64 +$

$2(35.45 + 1)$ or $208.33 + 98.07 = 233.5 + 72.9$;

which expresses a definite relation by weight. We do not know the absolute weight of a molecule but we do know very accurately their relative weights; so that these proportions are true when expressed in parts by weight; and, whatever the unit of the system may be, grains, grams, pounds, or tons, we shall always have 233.5 parts of barium sulphate and 72.9 parts of hydrochloric acid formed by the action of 208.33 parts of barium chloride on 98.07 parts of sulphuric acid.

Besides showing the products of the reaction and the relations by weight, the equation also represents relations of energy and heat absorbed or evolved. These will be discussed so far as they relate to analytical calculations in subsequent chapters.

Suppose the percentage of SO_3 is desired in magnesium sulphate. The salt is dissolved, barium chloride added and the resulting barium sulphate weighed. According to the preceding reaction, for every molecule of SO_3 present there will be a molecule of $BaSO_4$ precipitated; hence to find the weight of SO_3, we have: molecular weight of $BaSO_4$: molecular weight of SO_3 : : actual weight of $BaSO_4$: corresponding weight of SO_3, or

$$233.5 : 80.07 :: \text{wt. } BaSO_4 : \text{wt. } SO_3$$

or $$\frac{\text{weight } BaSO_4 \times 80.07}{233.5} = \text{weight } SO_3$$

and to get percentage we have:
weight taken for analysis (magnesium sulphate) : 100 : : weight SO_3 : x

or $$\frac{\text{weight } SO_3 \times 100}{\text{weight taken}} = \text{percentage of } SO_3. \ (*)$$

In the same way this precipitate of $BaSO_4$ can be used to determine the percentage of barium or barium oxide, here we have for barium: molecular weight of

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(*) When the magnesium sulphate is dissolved in water it is partly dissociated into Mg and SO_4 ions which react with the Ba and Cl ions, so the statement "molecule of SO_3 present in solution" is not literally correct but should be SO_4 ions corresponding to molecules of SO_3. This does not however affect the truth of the proportions given.

$BaSO_4$: atomic weight Ba : : weight $BaSO_4$: weight Ba, and for barium oxide:
mol. wt. $BaSO_4$: mol. wt. BaO : : wt. $BaSO_4$: wt. BaO.
or 233.5 : 153.43 : : wt. $BaSO_4$: x.

$$\text{and } \frac{x}{\text{wt. taken for analysis}} \times 100 = \text{Percentage BaO.}$$

If in this same precipitate the sulphur is desired (for example in coal analysis) we have

233.5 : 32.07 : : wt. $BaSO_4$: x (wt. S.)

The calculation for lead sulphate will be similar, though the proportion will be different on account of the higher atomic weight of lead. To calculate the weight of lead corresponding to one gram of $PbSO_4$ we have:

302.99 (Mol. wt. $PbSO_4$) : 206.92 (At. wt. Pb) : : 1 : x.
x = 0.6829.

Suppose we precipitate $MgNH_4PO_4 . 6H_2O$, filter, wash, ignite, and weigh. On ignition this is converted into magnesium pyrophosphate, $Mg_2P_2O_7$, which can be used either for the determination of magnesium oxide or phosphoric anhydride. We have the reactions:

$$MgCl_2 + NH_4OH + Na_2HPO_4 = MgNH_4PO_4 + 2NaCl + H_2O.$$

$$\text{and, } 2MgNH_4PO_4 + \text{heat} = Mg_2P_2O_7 + 2NH_3 + H_2O.$$

For every molecule of the ignited precipitate there must have been present in the original solution two atoms of magnesium, two atoms of phosphorus or one molecule of P_2O_5; so to get the corresponding amount of MgO we have:

Mol. wt. $Mg_2P_2O_7$: 2 (Mol. wt. MgO) : : wt. ppt. : x.
or 222.6 : 80.58 : : wt. ppt. : x.

$$\text{and } \frac{x}{\text{wt. taken}} \times 100 = \text{Percentage of MgO.}$$

Similarly to get the corresponding weights of phosphorus or phosphoric anhydride we have:

$Mg_2P_2O_7 : 2P :: \text{wt. ppt.} : x.$

$222.6 : 62.02 :: \text{wt. ppt.} : x.$

and $Mg_2P_2O_7 : P_2O_5 :: \text{wt. ppt.} : x.$

$222.6 : 142.02 :: \text{wt. ppt.} : x.$

The calculations for the pyrophosphates of zinc and of manganese are similar, using the atomic weights of these metals instead of that of magnesium.

Zinc is often weighed as $ZnNH_4PO_4$: in this case for each molecule of the precipitate there will be but one zinc and the proportion will be

$175.5 : 65.41 :: \text{wt. ppt.} : x.$

All direct stoichiometrical calculations are made in this way, using the proper atomic weights and bearing in mind to place in the proportion the weight of the number of atoms or molecules of the constituent sought, which the precipitate or the residue weighed contains.

Indirect Determinations.—In the material weighed the element to be determined may not be present at all.

For example: Potassium is precipitated quantitatively as K_2PtCl_6: this may be weighed as such or may be ignited with a little oxalic acid, the soluble potassium chloride washed out, and the spongy platinum weighed. The reactions are

$$2KCl + H_2PtCl_6 = K_2PtCl_6 + 2HCl.$$

To calculate the weight of K_2O from the weight of the double chloride we have

$\text{Mol. wt. } K_2PtCl_6 : \text{Mol. wt. } K_2O :: \text{wt. ppt.} : x.$

$485.81 : 94.22 :: \text{wt. ppt.} : x.$

If platinum is weighed:—each molecule of K_2PtCl_6 has one atom of platinum and two of potassium, so for each atom of platinum weighed there must have been two atoms of potassium, equivalent to a molecule of K_2O in the solution to cause its precipitation, hence we have

At. wt. Pt : Mol. wt. K_2O : : wt. residue : x
or 194.89 : 94.22 : : wt. residue : x

and in either case $\frac{x}{\text{wt. taken}} \times 100$ = Percent of K_2O.

It must always be kept in mind that, when there is a change in composition during ignition, it is the formula of what is actually weighed which gives the basis for calculation. For example, cobalt is often separated from nickel by precipitation as $2Co(NO_2)_3, 6KNO_2$ and after filtering, etc., is converted into $CoSO_4$ and K_2SO_4 by sulphuric acid. The properties of the double nitrite are studied for the purpose of separation but all calculations are based on the sulphates weighed. To illustrate: One gram of nickel matte was taken for analysis and the mixed sulphates of cobalt and potassium weighed 0.0896 gram. What is the percentage of cobalt? We have the reaction,

$$2Co(NO_2)_3, 6KNO_2 + 5H_2SO_4 = 2CoSO_4 + 3K_2SO_4 + 5H_2O + 7NO_2 + 5NO.$$

so for every $2CoSO_4 + 3K_2SO_4$ there must be 2Co or
832.87 : 117.86 : : 0.0896 : x. x = 0.0126 gram or 1.26% Co.

QUANTITY OF REAGENTS.

In analytical as well as technical work it is often necessary to know what quantity of a reagent to add to cause a reaction.

For example. How much 4% ammonium oxalate is necessary to precipitate as calcium oxalate the lime in one gram of limestone? We have the reactions;

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$$
$$CaCl_2 + (NH_4)\,C_2O_4 = CaC_2O_4 + 2NH_4Cl.$$

We see by comparing the two equations that one molecule of $CaCO_3$ requires one of $(NH_4)C_2O_4$. So, assuming that the limestone is pure calcium carbonate, we have; Mol. wt. $CaCO_3$: Mol. wt. $(NH_4)\,C_2O_4$: : wt. limestone : wt. ammonium oxalate or

$$100.09 : 126.16 :: 1 : x. \quad x = 1.2404 \text{ grams},$$

but a 4% (by weight) solution is to be used; to find what weight of solution contains 1.2404 grams of the salt we have

$$1.2404 : x :: 4 : 100. \quad x = 31.01 \text{ grams}.$$

It is not to be inferred that this is necessarily the best amount to add but it is certain that less will be insufficient for complete precipitation.

In the precipitation of zinc as zinc ammonium phosphate, it is considered advisable to add three times the amount of the precipitant actually required. How many grams of a 15% solution of NH_4NaHPO_4 should be added to a solution containing 0.25 gram of zinc? The reaction is:

$$Zn(NO_3)_2 + NH_4NaHPO_4 + NH_4OH. =$$
$$ZnNH_4PO_4 + NH_4NO_3 + NaNO_3 + H_2O$$

or one molecule of precipitant for one atom of zinc: Hence to satisfy the equation 0.5245 gram are required for,

$$137.15 : 65.41 :: x : 0.25. \quad x = 0.5245.$$

The corresponding weight of a 15% solution is 3.496 grams, for

$$0.5245 : x :: 15 : 100. \quad x = 3.496.$$

This is the weight of a 15% solution necessary to satisfy the equation but we are to add three times this amount or 10.488 grams.

To obtain a 15% solution of the active constituent: Microcosmic salt contains four molecules of water of crystallization, so to make—say 100 grams of a 15% solution we must first find what weight of the crystallized salt is required to give 15 grams of the active constituent.

Mol. wt. $NaNH_4HPO_4$: Mol. wt. $NaNH_4HPO_4 . 4H_2O$: : 15 : x or 137.15 : 165.17 : : 15 : x. x = 18.064.

So we must weigh out 18.064 grams and dissolve it in 100–18.064 grams or 81.936 grams of water.

TO DETERMINE WHICH REAGENT IS MOST ECONOMICAL.

Cases often arise where a reaction can be performed by several reagents, so that it is of importance to use the most economical, not necessarily the lowest priced. For example, which is more economical as an oxidizing agent, potassium chlorate at 8 cents a pound or sodium chlorate at 10 cents?

One molecule of either will yield three atoms of oxygen, so the oxygen in a pound of $KClO_3$ is $\frac{48}{122.56}$ lb. and the oxygen in a pound of $NaClO_3$ is $\frac{48}{106.5}$ lb. The most economical is the one which gives the most oxygen for one cent. To compare these we have,

$KClO_3$ $\frac{48}{122.56} \div 8$ or 0.04895 lb. for one cent.

$NaClO_3$ $\frac{48}{106.5} \div 10$ or 0.04507 lb. for one cent.

Which shows potassium chlorate to be more economical at the prices given.

EXAMPLES.

1. What is the weight of BaO in 1.9327 grams of $BaCrO_4$? *Ans.* 1.1694.

2. What is the weight of CaO in 2.9478 grams of $CaSO_4$? *Ans.*. 1.2142.

3. What weight of $MnCO_3$ yields on ignition 1.450 grams of Mn_3O_4? *Ans.* 2.1847.

4. How much arsenic is there in 5 grams of As_2S_3? of As_2S_5? of $Mg_2As_2O_7$?
Ans. (a) 3.0463, (b) 2.4167, (c) 2.4151.

5. How much AgI can be made from a pound of pure silver? How much AgBr? How much AgCl?
Ans. 2.1754 lbs. AgI, 1.7409 lbs. AgBr, 1.3285 lbs. AgCl.

6. 1.10 grams of stibnite gave on analysis 0.5987 gram of Sb_2O_4. What is the percentage of antimony? *Ans.* 43%.

7. How many pounds of water will it take to slack 100 lbs of quicklime (CaO)? *Ans.* 32.13 lbs.

8. How many pounds of red lead (Pb_3O_4) can be made from a ton of litharge (PbO)? *Ans.* 2048 lbs.

9. How many grams of MnO_2 and of H_2SO_4 are required to give 10 grams of oxygen?
Ans. 61.306 grams H_2SO_4, 54.37 grams MnO_2.

10. One gram of coal gave 0.2634 gram of $BaSO_4$ by Eschka's Method; 1 gram of MgO and 0.5 gram of

Na_2CO_3 were used. It was found that both contained sulphur: 10 grams of MgO and 5 grams of Na_2CO_3 (together) gave 0.1654 gram of $BaSO_4$. What is the percentage of sulphur in the coal? *Ans.* 3.39%.

11. How many pounds of 20% H_2SO_4 will it take to neutralize a ton of Na_2CO_3? of $NaHCO_3$? of $CaCO_3$?
Ans. (a) 9244 lbs., (b) 5833.5 lbs., (c) 9800 lbs.

12. How many pounds of 10% HCl will it take to neutralize a ton of Na_2CO_3? of $NaHCO_3$? of $CaCO_3$?
Ans. (a) 13744 lbs., (b) 8673 lbs., (c) 14571 lbs.

13. Suppose one gram of silver is dissolved in nitric acid and to it is added 0.25 gram of pure dry sodium chloride. What percentage of the silver remains in solution? *Ans.* 53.88%.

14. Suppose 0.25 gram of sodium bromide were added to a solution of one gram of silver. What percentage of silver remains in solution?
Ans. 73.81%.

15. A dolomite contains 98% of calcium and magnesium carbonates, 2% of SiO_2 and 10% of MgO. What is the percentage of CO_2? *Ans.* 44.81%.

16. One gram of ore containing nickel and cobalt gave 0.2750 gram of metallic nickel and cobalt and 0.2103 gram of sulphates of potassium and cobalt ($3K_2SO_4, 2CoSO_4$) What is the percentage of nickel?
Ans. 24.52%.

17. One gram of a rock gave on analysis, combined sodium and potassium sulphates 0.150 gram and platinum from K_2PtCl_6 0.1127 gram. What are the percentages of K_2O and Na_2O?
Ans. K_2O 5.45%. Na_2O 2.15%.

18. In an iron ore, ferric oxide, alumina and phosphoric acid were precipitated together, ignited and

weighed as Fe_2O_3, Al_2O_3 and $FePO_4$. The weight from three grams of ore was 2.4750 grams: the iron was found to be 50.5% and the phosphorus 0.25%. What is the percentage of Al_2O_3? *Ans.* 9.80%.

19. Which is more economical for neutralizing an alkali 60% HNO_3 at 6 cents per pound, or 20% HCl at 3 cents per pound? *Ans.* HCl.

20. Which is the more economical oxidizing agent KNO_3 at 5 cents a pound or $NaNO_3$ at 5½ cents a pound? *Ans.* $NaNO_3$.

CHAPTER V.

CALCULATION AND USE OF FACTORS.

In gravimetric analysis factor means the number by which the weight of any precipitate or residue is multiplied to give the weight of the constituent desired, whether the constituent is actually present or has previously been combined in a known proportion.

To calculate the factor for SO_3 in $BaSO_4$ we have

$$x : 1 : : \text{Mol. wt. } SO_3 : \text{Mol. wt. } BaSO_4 \text{ or}$$

$$\frac{\text{Mol. wt. } SO_3}{\text{Mol. wt. } BaSO_4} \text{ or } \frac{80.07}{233.50} \text{ or } 0.3429.$$

The factor is the weight of SO_3 in one gram of $BaSO_4$ or one hundreth of the percent of SO_3 in $BaSO_4$.

To calculate the factors for S and for BaO, we have

$$\frac{32.07}{233.50} = 0.1373 \text{ and } \frac{153.43}{233.50} = 0.6571.$$

Factors are used as follows:—

First, To simplify calculations.

Instead of making the proportion—

Mol. wt. $BaSO_4$: Atomic wt. S : : wt. $BaSO_4$: wt. S. we have wt. $BaSO_4 \times$ factor (0.1373) = wt. S. So that if we have a table of factors, the calculation requires only one multiplication, and this can be changed into an addition by the use of logarithms.

These tables will be found at the back of the book.

Second, To avoid or to greatly reduce calculation by weighing out a multiple of the factor for analysis.

If the weight taken in grams equals the factor each milligram of precipitate or residue equals 0.1% without any calculation. When ten times the factor is taken each milligram equals 0.01%. When one hundred times the factor is used each milligram equals 0.001% and so on.

This can be proved as follows:—

Suppose we are to determine SO_3 in crystallized magnesium sulphate, $MgSO_4,7H_2O$. Weigh out for analysis 3.4291 grams (ten times the factor), dissolve, and then precipitate as $BaSO_4$, in the usual way; the precipitate weighed 1.626 grams, then we have

$$\frac{1.626 \times 0.3429}{3.429} \times 100 = \text{Percentage of } SO_3$$

but 0.3429 goes into 3.429 ten times and 10 into 100 ten times, so the result in percentage is ten times the weight in grams or 16.26%, or the precipitate contained 1626 milligrams, each of which is therefore equivalent to 0.01%.

Again the factor for S in $BaSO_4$ is 0.13734. If we weigh out 13.734 grams of pig iron for analysis, each milligram of $BaSO_4$ will be equivalent to 0.001% S. For suppose the $BaSO_4$ obtained, weighed 0.0270 gram; we would have

$$\frac{0.027 \times 0.13734}{13.734} \times 100 = \text{Percent. of S or } 0.027\%.$$

So 27 milligrams = 27 thousandths percent or each milligram = 0.001 percent. But this is too large an amount to take unless the sulphur is extremely low, so in practice some portion of it is used as ½, ⅓ or 0.4; then the weight of $BaSO_4$, expressed in grams, times 2, 3, or 2.5 is the percentage of sulphur without any further calculation. For example, if for the determination of sulphur, 5.4936 grams is taken, the weight of $BaSO_4$ in grams divided by four and multiplied by ten gives the percentage of sulphur, for the weight 5.4936 is forty times the factor for S in $BaSO_4$. Suppose the actual weight of $BaSO_4$ to be 0.200 gram, then

$$\frac{0.200 \times 0.13734}{5.4936} = 0.005 \text{ wt. S in one gram,}$$

and this times 100 gives percentage or 0.5%;

which result is $\frac{0.200}{4} \times 10 = 0.5\%$.

Inasmuch as these relations are confusing at first, especially when the weights of precipitates are sometimes given in grams, and sometimes in milligrams, the following table may prove useful.

Weight taken in Grams.	Weight Precipitate in Grams.	Weight Precipitate in Milligrams.
Factor	Times 100 = Percent	Divided by 10 = Percent Each Mg. = 0.1%
Factor × 5.	Times 20 = Percent	Divided by 50 = Percent Each Mg. = 0.02%
Factor × 10	Times 10 = Percent	Divided by 100 = Percent Each Mg. = 0.01%
Factor × 50	Times 2 = Percent	Divided by 500 = Percent Each Mg = 0.002%
Factor × 100	Percent Direct	Divided by 1000 = Percent Each Mg = 0.001%

The use of factors to save time should not be pushed too far, as the time taken in obtaining an exact quantity of some crystallized salts or of drillings may be greater than that saved in calculation. The examples given have that objection, which however would not apply to an iron ore or coal in which sulphur was to be determined, as the sample would be in a finely pulverized condition. It takes but little longer to weigh out, say exactly 1.3734 grams than exactly one gram, for the time is consumed in getting the exact weight, not in putting the weights on the pan: and when an analysis is repeatedly made, even this time can be saved by using a special weight, the most convenient multiple of the factor.

This system can be very easily applied also to volumetric work, here the amount to be weighed out will be a multiple of the standard (titer) of the solution used. Suppose we have a solution of $KMnO_4$ 1 c.c. = 0.0056 gram of iron. If we take for analysis 0.56 gram of iron ore and 55.1 c.c. of $KMnO_4$ are used, the ore contains 55.1% of iron for

$$\frac{55.1 \times 0.0056}{0.56} \times 100 = 55.1\%.$$

So that when we take for the test a weight equal to hundred times the standard of the solution, each cubic centimeter equals one percent and the burette reading gives percentage direct.

One hundred times the standard may not be the most convenient quantity to take, but this can be readily be adjusted to the particular titration, bearing in mind that, when

50 times the standard is taken 1 c.c. = 2%.
100 " " " " 1 c.c. = 1%.
200 " " " " 1 c.c. = 0.5%.

and so on.

The plan of adjusting the weight taken to the strength of the solution presents many advantages over the system of adjusting the solution to a certain weight for analysis, when a portion is used for a single determination. This is particularly the case when the standard solution changes in strength and has to be frequently restandardized. If we always use one burette, which is uniformly calibrated, for the particular solution and weigh out a multiple of the standard for analysis, that burette will read percentage: and we do not have to make up the solution to a certain arbitrary strength, which necessitates accurate measuring apparatus, flasks, etc., which agree with the burette. Then if on standing the solution evaporates or undergoes a partial decomposition, it must be readjusted to read percentage when an arbitrary weight is taken, while by weighing out a multiple of the new standard much trouble is saved with no sacrifice of accuracy. It is not to be inferred however that this system is advantageous in all cases, but only for separate determinations such as iron, copper, zinc, etc.

The most important application of the use of factors, is the assay ton system devised by Prof. Chandler. In assaying ores of gold and silver, the precious metals are always reported in ounces Troy per ton of 2000 pounds avoirdupois. If a suitable number of grams, twenty-five for instance, is taken and the gold and the silver weighed in milligrams, a long calculation is required to convert the results to ounces per ton. If however an assay ton 29.1666 grams, is used, the result in gold or silver as weighed in milligrams is ounces to the ton without any calculation.

The assay ton is derived as follows:—

One pound avoirdupois contains 7000 grains.
One ton, 2000 lbs., contains 14,000,000 grains.
One ounce Troy contains 480 grains.

Therefore 14,000,000 ÷ 480 or 29,166.6 is the number of Troy ounces in 2000 lbs. avoirdupois; so if we take this number of milligrams for assay (29,166.6 +), each milligram of gold or of silver found is an ounce Troy to the ton in the ore: for

$$1 : 29{,}166.6 + :: 480 : 14{,}000{,}000.$$

Therefore the assay ton is 29,166.6 + milligrams or 29.1666 + grams.

EXAMPLES.

1. Calculate the factors for Na_2O in Na_2SO_4 and in NaCl. *Ans.* 0.4368 and 0.5308.

2. Calculate the factors for Zn in ZnO, in $ZnNH_4PO_4$ and in $Zn_2P_2O_7$.
Ans. 0.80346, 0.3664 and 0.4291.

3. Calculate the factors for As in As_2S_3, in $Mg_2As_2O_7$ and Ag_3AsO_4. *Ans.* 0.6092, 0.4830 and 0.1621.

4. Calculate the factors for **N**, NH_3 and NH_4Cl, for weight of platinum from ignition of $(NH_4)_2PtCl_6$.
Ans. 0.1441, 0.1751 and 0.54925.

5. What are the factors for conversion of Cr into Cr_2O_3, into $PbCrO_4$ and into $BaCrO_4$?
Ans. 1.4603, 6.1960 and 4.8632.

6. (a) What is the factor to convert weight of $BaSO_4$ to corresponding weight of H_2SO_4?

(b) What is the factor to convert percentage of K_2O to percentage of K_2SO_4?
Ans. (a) 0.42007. (b) 1.8498.

7. What are the factors for K_2O and for KCl in platinum from K_2PtCl_6?
Ans. 0.48345 and 0.76515.

8. What are the factors for the iron in Fe_2O_3 and in Fe_3O_4? *Ans.* 0.7001 and 0.7242.

9. One gram of an antimony ore was taken for analysis and the Sb_2O_4 resulting weighed 0.3478 gram:

by mistake the factor for Sb_2S_3 was used. What was the error in percentage of antimony? *Ans.* 2.626%.

10. An alloy contains 10% of antimony. One gram of this alloy gives 0.2895 gram of combined oxides of antimony and tin (Sb_2O_4 and SnO_2). What would be the error in percentage of tin if only the factor for Sb_2O_4 were used in the calculation? *Ans.* 0.032%.

11. What weights of spiegel must be taken for analysis so that each milligram of $Mn_2P_2O_7$ shall equal respectfully 0.2%, 0.1% and 0.05%? *Ans.* 0.1936, 0.3872 and 0.7744.

12. What weights of sphalerite must be used so that each milligram shall equal 0.1% when the zinc is weighed as ZnO, as $ZnNH_4PO_4$ and as $Zn_2P_2O_7$? *Ans.* 0.8035, 0.3664 and 0.4291.

13. What weight of steel must be taken so that, when the phosphorus is weighed as $Mg_2P_2O_7$, the weight in grams shall be percentage direct? *Ans.* 27.8681.

14. What weight of pig iron must be taken so that the weight of $BaSO_4$ in grams shall be percentage of sulphur when multiplied by three. *Ans.* 4.5780.

15. What weights of lead ore must be used so that each milligram of $PbSO_4$ shall equal 0.05%, 0.1% and 0.2%? *Ans.* 1.3658, 0.6829 and 0.3415.

16. What weights of limestone must be taken so that each milligram of CaO equals 0.1% of CaO? So that each milligram of $CaSO_4$ equals 0.1% of CaO? *Ans.* 1 and 0.4119.

17. Given a solution of $K_2Cr_2O_7$, 1 c.c. = 0.0054 gram of iron. How much ore must be taken so that each c.c. shall read 0.1%, 0.2%, 0.3%, 0.5%, 0.7% and 1.%? *Ans.* 5.4, 2.7, 1.8, 1.08, 0.7714, 0.54.

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18. Given a solution of $K_4Fe(CN)_6$, 1 c.c. = 0.00896 gram of zinc. How much ore must be taken so that each c.c. shall equal 2%, 1%, 0.5%, 0.1%?

0.4480, 0.8960, 1.792, 8.960.

19. Calculate the ounces Troy per ton avoirdupois in the following—

(a) One tenth assay ton of copper matte gave gold 1.22 mgs., silver 30.94 mgs.

(b) Four assay tons of siliceous ore gave gold 0.12 mg., silver 0.52 mg.

(c) One sixth assay ton of a zinc blende gave gold 0.02 mg., silver 37.72 mgs.

Ans.:

(a)	(b)	(c)
12.2 ozs. Au.	0.03 oz. Au.	0.12 oz. Au.
309.4 ozs. Ag.	0.13 oz. Ag.	226.32 ozs. Ag.

20. Calculate the number of grams in an assay ton for a long ton (2240 pounds).

Ans. 32.6666 grams.

CHAPTER VI.

CALCULATIONS OF VOLUMETRIC ANALYSIS.

NORMAL SOLUTIONS.

A normal solution is one which contains the hydrogen equivalent of the active constituent in grams per liter. That is, the amount in a liter which brings into reaction 1.008 grams of hydrogen, 8 grams of oxygen or their equivalents, whether the reaction be one of oxidation, reduction, precipitation or saturation.

This definition is used by Mohr and by Sutton and is also in very general use in America. In the examples given in this book this system is used. There are however other definitions of normal solutions, which have caused considerable confusion. They are:

First. The molecular weight in grams per liter. This definition possesses some advantages, for example according to Mohr's definition we can have two normal solutions of $KMnO_4$ of different strengths depending on whether it is used in a neutral or in an acid solution; while according to the "molecular weight in grams" this can not happen, on the other hand Mohr's definition has the great advantage that all normal solutions are equivalent cubic centimeter for cubic centimeter. Solutions containing the molecular weight in grams per liter are now much used in physical chemistry under the name gram-molecule.

Second. In the Gay-Lussac method for the determination of silver, used in mints and assay offices, normal salt solution is the name given to a solution of such strength that one hundred cubic centimeters will exactly precipitate one gram of silver. This is a special use of the word normal and should not be connected in any way with the equivalent system of volumetric analysis.

Under the system we have adopted, it is absolutely essential to have a correct understanding of "the hydrogen equivalent in grams." Suppose we wish to make a normal solution of sodium hydroxide; we have the reaction—

$$NaOH + HCl = NaCl + H_2O.$$

What is the amount necessary to bring into reaction one equivalent of hydrogen? Evidently the molecular weight in grams of NaOH (40.06) for this is the amount necessary to react with 36.46 grams of HCl and so bring into reaction 1.008 grams of hydrogen.

If we wish a normal solution of Na_2CO_3 we have $Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2$. It is evident that one molecule of Na_2CO_3 brings into reaction two atoms of hydrogen, hence a normal solution of Na_2CO_3 will be one half of the molecular weight or 53.05 grams per liter.

Similarly a normal solution of hydrochloric acid will contain the molecular weight, 36.46 grams per liter, of sulphuric acid one half the molecular weight, 49.043 grams, and of orthophosphoric acid one third the molecular weight in grams or 32.68 grams.

One cubic centimeter of any of these acid solutions will exactly saturate one cubic centimeter of any of the alkaline solutions.

In reactions of precipitation the same rule applies we have,—

$$AgNO_3 + HCl = AgCl + HNO_3 \text{ or}$$
$$AgNO_3 + NaCl = AgCl + NaNO_3$$

A normal solution of silver nitrate contains the molecular weight in grams, 169.96, per liter: for according to the first reaction 1.008 grams of hydrogen would be actually brought into reaction by a liter of this solution and in the second, the weight of sodium equivalent to 1.008 grams of hydrogen. Similarly with, $NH_4SCN + AgNO_3 = AgSCN + NH_4NO_3$, a normal solution will contain the molecular weight of ammonium thiocyanate in grams per liter or 76.19 grams. To precipitate a salt of a diatomic element such as $BaCrO_4$, we have a normal solution equal to one half the molecular weight in grams per liter; for K_2CrO_4, 97.18 grams; for Na_2CrO_4, 81.12 grams.

For convenience we designate a normal solution by N, tenth normal by $^N/_{10}$, one hundreth normal by $^N/_{100}$ and so on.

In the original definition of normal solution appears "equivalent to one gram of hydrogen." This can be retained with perfect accuracy if the atomic weights used are calculated on the basis of hydrogen as unity; but as the ratio of hydrogen to oxygen has been found to be 1 : 15.88 and not 1 : 16 we must adopt either $H = 1$ or $O = 16$ as a basis. $O = 16$ is most generally used at present so to make our definition of normal comparable with the present atomic weights, instead of equivalent to one gram of hydrogen, we must substitute, equivalent to 1.008 grams of hydrogen or better equivalent to 8 grams of oxygen. The advantage of the latter definition will appear in the following explanations of normal solutions for oxidation and reduction.

When ferrous iron is oxidized by potassium dichromate we have the reaction $K_2Cr_2O_7 + 3Fe_2Cl_4 + 14HCl = 3Fe_2Cl_6 + 2KCl + Cr_2Cl_6 + 14H_2O$: the essential oxidation in this reaction can be expressed as follows—

$6FeO + 3O = 3Fe_2O_3$. Three atoms of oxygen from the $K_2Cr_2O_7$ oxidize six atoms of ferrous iron as chloride to the ferric condition, or in other words an iron requires one half an oxygen, equivalent to one hydrogen: so for a normal solution, the molecular weight of $K_2Cr_2O_7$ in grams must be divided by six, since each molecule oxidizes six atoms of iron each equivalent to one atom of hydrogen or one half an atom of oxygen, or expressed in the form of a proportion we have—

Mol. wt. $K_2Cr_2O_7 : x :: 3 \times 16 : 8$. $x = 49.083$ grams.

With $KMnO_4$ we have $2KMnO_4 + 5Fe_2(SO_4)_2 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$.

The essential oxidation is $Mn_2O_7 + 10FeO = 5Fe_2O_3 + 2MnO$ or $2KMnO_4$ give 5 oxygen. To calculate the oxygen equivalent we have, 2 (Mol.Wt. $KMnO_4$) $= 316.2$ grams, gives oxygen, $5 \times 16 = 80$ grams, hence $316.2 : x :: 80 : 8$ or a normal solution of $KMnO_4$ contains 31.62 grams per liter when used in an acid solution.

In the Volhard method for manganese we have in a neutral solution the following reaction

$$2KMnO_4 + 3MnSO_4 + 2ZnO = 5MnO_2 + K_2SO_4 + ZnSO_4$$

the essential oxidation is $Mn_2O_7 + 3MnO = 5MnO_2$ or two molecules of $KMnO_4$ give up under these conditions three atoms of oxygen, so to get a normal solution we have $316.2 : x :: 48 : 8$ or

$$x = \text{Mol.Wt} \div 6 = 52.7 \text{ grams per liter.}$$

This is one of the very few cases where the molecular weight definition of normal seems preferable, as here we have two normal solutions of different strengths depending on the reaction. As permanganate is usually used in an acid solution, unless expressly stated, normal means 31.62 grams per liter.

Normal reducing solutions are not much employed, but the following will serve as an illustration. We have the reaction

$$SnCl_2 + Fe_2Cl_6 = SnCl_4 + Fe_2Cl_4:$$

one molecule of $SnCl_2$ removes two atoms of chlorine or what is the same thing reduces two atoms of iron to the ferrous condition. Now two chlorine correspond to one oxygen; hence one half the molecular weight in grams of stannous chloride will give a normal solution or

$$189.95 : x :: 16 : 8. \quad x = 94.975 \text{ grams.}$$

To ascertain the strength of any normal solution the reaction in which it is to be used must always be considered and in this way all confusion will be avoided.

An advantage of the "equivalent" definition of normal, which deserves attention, is that when the formula of a compound is altered the equivalent is not; so that whether you consider potassium permanganate as $K_2Mn_2O_8$ or $KMnO_4$, arsenious oxide as As_2O_3 or As_4O_6 or ferric chloride as Fe_2Cl_6 or $FeCl_3$, the number of grams per liter of a normal solution will remain the same. This is made clear by the following reactions.

$$K_2Mn_2O_8 + 10FeSO_4 + 8H_2SO_4 = \\ 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

Now written

$$2KMnO_4 + 5Fe_2(SO_4)_2 + 8H_2SO_4 = \\ 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

In either case the same weight of potassium permanganate oxidizes the same weight of iron and normal solutions will be identical for N $K_2Mn_2O_8$ will be one tenth the molecular weight, 31.62 grams, and N $KMnO_4$ one fifth, 31.62 grams. The same applies to ferrous sulphate.

In using normal solutions the following rules are important. Weigh out one-tenth the equivalent in grams of the substance to be determined and the burette reading gives the percentage directly. With N/10 solutions weigh out one hundreth of the equivalent in grams and the burette shows the percentage directly. To make this clear, suppose we have a normal sulphuric acid solution and we wish to titrate a sample of caustic potash and to express the results in percentage of K_2O. N H_2SO_4 contains $\frac{98.09}{2}$ grams per liter or 1. c.c. = 0.049045 gram of H_2SO4. The equivalent of K_2O is $\frac{94.22}{2}$ or 47.11; so N H_2SO_4 is equivalent to 0.04711 gram K_2O per c.c. One-tenth the equivalent in grams, 4.711, is weighed out, dissolved and titrated, requiring 78.2 c.c. of N H_2SO_4. Obtain the percentage by going through the ordinary calculation

$$\frac{78.2 \times 0.04711}{4.711} \times 100 = 78.2\%.$$

It is seen that this is only another way of expressing the fact that when one hundred times the standard is taken for analysis, the burette gives percentage direct.(*)

Besides normal solutions we have standard solutions, that is solutions of known strength. Normal solutions are always standard but standard solutions are not always normal. The salt solution used in the mints is standard, but only normal in a particular sense of the word. Most of the solutions used in volumetric analysis are standard and only approximately normal, tenth normal or one hundreth normal. The question of the strength of solutions and whether systematic or not is largely a matter of individual preference, limited by the

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(*) A table of the more common N and N/10 solutions will be found at the back of the book.

solubility of the reagent and the requirements of the particular analysis to be performed.

In the calculations of volumetric as in gravimetric analysis the basis of calculation is an equation. Unfortunately there are some cases in which the reaction can not be expressed by a simple equation and in these cases standard not normal solutions must be used.

ALKALIMETRY AND ACIDIMETRY.

Many of these calculations require no special mention here as they can readily be performed after the explanations already given. Only a few special cases are given in detail.

In order not to complicate these calculations by the use of different indicators, phenolphtalein is used throughout. This indicator acts as follows:

Red with fixed alkalies, colorless with acids, including carbonic. So when acid is run into carbonated alkali the color is discharged when the Na_2CO_3 is converted into $NaHCO_3$, but on boiling the color returns due to the formation of more Na_2CO_3 from the $NaHCO_3$, so to get total Na_2CO_3, acid must be run in till the solution remains colorless on boiling. The reactions are

$Na_2CO_3 + HCl = NaHCO_3 + NaCl$ and (boiling)
$NaHCO_3 + HCl = NaCl + CO_2 + H_2O$.

1. Caustic and Carbonated Alkali.

1.5 grams of impure caustic potash are dissolved in water, diluted, an excess of barium chloride added and diluted to 400 c.c. One hundred cubic centimeters are filtered off and titrated with N HCl, 5.4 c.c. required. Another 1.5 grams of the sample dissolved and titrated directly with N HCl boiling, for total alkalinity, required 24.6 c.c. What are the weights of KOH and of K_2CO_3? The first titration gives the caustic alkali in $\frac{1.5}{4}$ grams, for the barium chloride precipitates the carbonate as barium carbonate and with the caustic gives equivalent amount of Ba $(OH)_2$, which is determined by the N HCl. The reactions are

$$Na_2CO_3 + BaCl_2 = BaCO_3 + 2NaCl \text{ and}$$
$$2NaOH + BaCl_2 = Ba(OH)_2 + 2NaCl$$

The total required	24.6 c.c.
The caustic required	21.6 c.c.
The carbonate required	3.0 c. c

N HCl = 0.05612 gram KOH per c.c.
= 0.06911 gram K_2CO_3 per c.c.

hence the weights are KOH, 1.2122 grams and K_2CO_3 0.2073 gram.

2. Carbonate and Bicarbonate.

Four grams of commercial sodium bicarbonate are titrated in a cold dilute solution with N/10 H_2SO_4 till the red color disappears: used 6.4 c.c.

To one gram of the sample dissolved in water, 20 c.c. of N H_2SO_4 are added and the solution boiled till all the carbonic acid is expelled, then titrated back with N KOH: requiring 8.1 c.c.

What are the percentages of $NaHCO_3$ and of Na_2CO_3?

The first titration shows one half of the Na_2CO_3, so for one gram the Na_2CO_3 required

$$\frac{2 \times 6.4}{4} = 3.2 \text{ c.c. of N/10 } H_2SO_4 \text{ or } 0.32 \text{ c.c. N } H_2SO_4.$$

The total Na_2O required 20–8.1 = 11.9 c.c. N H_2SO_4 so the N H_2SO_4 used on the Na_2O present as $NaHCO_3$ was 11.9 – 0.32 = 11.58 c.c.

The weights corresponding are

$$\begin{aligned} \text{NaHCO}_3 \quad 11.58 \times 0.08406 &= 0.9734 \text{ gram} \\ \text{Na}_2\text{CO}_3 \quad 0.32 \times 0.053 &= 0.0169 \text{ gram} \end{aligned}$$

or 97.34% $NaHCO_3$ and 1.69% Na_2CO_3.

3. Phosphorus from Ammonium Phospho-Molybdate.

The phosphorus is precipitated as $(NH_4)_3PO_4, 12MoO_3$, under carefully regulated conditions, this is dissolved in a standard alkali solution according to the reaction;

$$\begin{aligned} &2(NH_4)_3PO_4, 12MoO_3 + 23Na_2CO_3 + H_2O = \\ &\quad 2(NH_4)_2HPO_4 + (NH_4)_2MoO_4 + 23Na_2MoO_4 + 23CO_2. \end{aligned}$$

In practice an excess of the standard Na_2CO_3 solution is added then the excess titrated using phenolphtalein as an indicator. The reason that two molecules of the precipitate require 23 and not 24 molecules of Na_2CO_3 is that the indicator changes color when two of the. three replaceable hydrogens of phosphoric acid have been substituted by alkali, which leaves (from two molecules) two NH_4 groups to combine with a molecule of MoO_3 thus leaving 23 instead of 24 molecules of MoO_3 to be neutralized by Na_2CO_3.

To calculate the grams per liter of Na_2CO_3 solution equivalent to one milligram of P_2O_5 per cubic centimeter, we have: 1.c.c. = 1 mg. 1 liter = 1 gram.
$2(NH_4)_3PO_4, 12MoO_3$ contain $1P_2O_5$ hence

$$\begin{aligned} \text{Mol. wt. } P_2O_5 &: 23(\text{Mol.wt.}Na_2CO_3) :: 1 : x \\ 142.10 &: 2440.3 :: 1 : x \\ &x = 17.180 \text{ grams per liter of } Na_2CO_3. \end{aligned}$$

4. Sulphuric and Nitric Acids in Mixed Acid.

The analysis of the waste mixed acid from nitrating is sometimes made as follows: 50 grams of the sample are diluted to a liter and 10. c.c. of this mixture are withdrawn by a pipette which in this case delivered an amount containing exactly 0.4976 gram of the original sample. The sulphuric acid in this is precipitated as $BaSO_4$ and weighed = 0.7093 gram.

Another portion is titrated for total acidity as follows: Of an approximately N NaOH solution (20.2 c c. = 0.98 gram H_2SO_4) 20.2 c.c. are run into a beaker and this is the neutralized by the diluted acid solution. (50 grams to liter.) Suppose 25.75 c.c. are required.

To calculate the percentage of H_2SO_4

$$\frac{0.7093 \times 0.42007}{0.4976} \times 100 = 59.88\%$$

To calculate the percentage of HNO_3

$$25.75 \text{ c.c.} = 20.2 \text{ c.c. NaOH} = 0.98 \text{ gram } H_2SO_4$$

First calculate the total acidity to H_2SO_4:

As 50 grams are contained in 1000 c.c. 25.75 c.c. contain 1.2875 grams for 50 : 1000 : : x : 25.75 or x = $\frac{25.75}{20}$ = 1.2875 grams. Hence the total acidity in terms of H_2SO_4 is $\frac{0.98}{1.2875} \times 100$ or 76.12% and 76.12% − 59.88% or 16.24% is the acidity due to nitric acid but expressed in terms of H_2SO_4. As 63.048 parts of HNO_3 are equivalent in power of neutralizing NaOH to 49.043 parts of H_2SO_4; to determine the percentage of HNO_3 we have: 16.24 : x : : 49.043 : 63.048. x = 20.87%.

So the composition of the waste acid is

H_2SO_4 59.88%, HNO_3 20.87%.

PERMANGANATE CALCULATIONS.

Suppose we have a N/5 solution of $KMnO_4$; to calculate its strength in terms of oxalic acid we have the reactions.

$$2KMnO_4 + 5Fe_2(SO_4)_2 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O.$$

We see that the same quantity of $KMnO_4$ is required for $5Fe_2(SO_4)_2$ as for $5H_2C_2O_4$; $5Fe_2(SO_4)_2$ contains 10 Fe so that as regards $KMnO_4$, $10 \times$ atomic wt. of Fe $=$ $5 \times$ Mol. wt. $H_2C_2O_4$ or we have, Fe standard (0.0112) : oxalic acid standard : : $10 \times 56.02 : 5 \times 90.03$ or

$$0.0112 : x : : 560.2 : 450.2. \quad x = 0.0090.$$

All these steps are not necessary however, all we need do is to consider the strength of $^N/_5$ oxalic acid, then this will be equivalent c.c. per c.c. with $^N/_5$ $KMnO_4$. From the reaction we see that one $H_2C_2O_4$ requires one O: therefore the amount necessary to bring into reaction eight grams of oxygen will be one half the molecular weight in grams per liter and for $^N/_5$ one tenth the molecular weight or 9.003 grams, so that 1 c.c. will be equal to 0.0090 gram.

To calculate the standard to CaO or Cd, we shall also have one tenth the molecular or atomic weights, because these are precipitated as oxalates whose composition is CaC_2O_4 and CdC_2O_4 and the oxalic acid determined; so that one molecule of oxalic acid corresponds to a molecule of CaO or an atom of Cd.

To calculate the strength of $^N/_5$ $KMnO_4$ in terms of molybdic oxide we have the oxidation of Mo_2O_3 to MoO_3 or two MoO_3 require 3 oxygen, and we have

$$288 : x : : 48 : 8. \quad x = 48.$$

Therefore N MoO_3 would have one third the molecular weight in grams per liter (48 grams) and $^N/_5$ one fifteenth (9.6 grams) per liter or 1 c.c. = 0.0096 gram MoO_3.

The determination of phosphorus by $KMnO_4$ is indirect for as the ratio of MoO_3 to P in the ammonium phospho-molybdate is 12 to 1, for every 144 × 12 grams of MoO_3 found by titration there must be 31 grams of phosphorus present: so we have MoO_3 standard : P standard as 1728 : 31 or 1 c.c. $^N/_5$ $KMnO_4$ =0.0001722 gram of phosphorus.

To calculate this value for a standard $KMnO_4$ solution not normal when the iron standard is known: we have

$$6KMnO_4 = 10MoO_3 \quad \text{and}$$
$$6KMnO_4 = 30\,Fe \quad \text{hence}$$

10 MoO_3 correspond to 30 Fe and the Fe standard: MoO_3 standard : : 1680 : 1440 * or as 7 : 6 and as the phosphorus standard is 1.794% of the MoO_3 standard, the phosphorus standard will be 6/7 of 1.794% of the Fe standard or the Fe standard times 0.01538.

A rather confusing calculation is met in the Ford-Williams method for manganese: here the manganese is precipitated as hydrated MnO_2 and its oxidizing power measured. Suppose we take for analysis one gram of pig iron, and to the precipitate of MnO_2 add 25 c.c. of $^N/_{10}$ $Fe_2(SO_4)_2$ and then titrate the $Fe_2(SO_4)_2$ remaining unoxidized by $^N/_{10}$ $KMnO_4$, using 12 c.c. What is the percentage of manganese?

The reactions are

$$MnO_2 + Fe_2(SO_4)_2 + 2H_2SO_4 = MnSO_4 + Fe_2(SO_4)_3 + 2H_2O.$$

and the usual reaction between the excess of ferrous sulphate and permanganate. The solutions used were both $^N/_{10}$ and therefore correspond c.c. for c.c., so that the oxidation done by the MnO_2 was equal to that which

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* According to the latest atomic weights this ratio should be 1680.6 : 1439.9.

would have been done by 13 c.c. of $^{N}/_{10}$ $KMnO_4$. Now we have

$$2KMnO_4 = 10Fe$$
$$1MnO_2 = 2Fe$$

Hence $2KMnO_4$ are equivalent to $5MnO_2$ or 5Mn, or Fe standard : Mn standard : : 560.2 : 274.95 and the percentage of manganese will be 13 (number of c.c of $KMnO_4$ *not* required)

$$\times 0.00275 \div 1 \times 100 \text{ or } 3.57\% \text{ Mn.}$$

Oxalic acid may be used in the same method instead of ferrous sulphate to measure the oxidizing power of the precipitate and the excess titrated by permanganate. Suppose one gram of spiegel is taken for analysis and that we have a $KMnO_4$ solution (not systematic) whose strength is 1.c.c. = 0.006 grams of iron. We make up a solution of oxalic acid and find that it requires 25 c.c. of the $KMnO_4$ solution to oxidize 20 c.c. of the oxalic acid solution. To the precipitate (hydrated MnO_2) from one gram of spiegel, 80 c.c. of the oxalic acid solution are added and, after the complete solution of the precipitate, the excess is titrated by $KMnO_4$, this requires 12.c.c. To calculate the percentage of manganese: If there had been no MnO_2 present the 80 c.c. of oxalic acid would have required 100 c.c. of $KMnO_4$, but only 12 were needed, therefore the oxidation done by the MnO_2 present was equal to that of 88 c.c. of $KMnO_4$. Now the manganese standard of our $KMnO_4$ is

$$0.006 : x : : 560.2 : 274.95 \quad \text{or } 0.002945$$

and $88 \times 0.002945 \div 1 \times 100 = 25.92$ the percentage of manganese.

The peculiar part of this method is that it is the amount of $KMnO_4$ not used which is the basis of calculation.

IODINE CALCULATIONS.

Tenth normal iodine solution, 12.685 grams per liter, can be used for a great many titrations. For example, in the determination of H_2S and so of sulphur in pig iron, &c. The reaction is

$$H_2S + 2I = S + 2HI.$$

Five grams of pig iron evolved, on treatment with hydrochloric acid, H_2S, which when titrated in a dilute solution with starch as indicator required 6.2 c.c. of $^N/_{10}$ iodine solution. What is the percentage of sulphur?

$^N/_{10}$ I = 0.012685 gram I per c.c. = 0.001603 gram S per c.c. $\frac{6.2 \times 0.0016}{5} \times 100 = 0.198\%$ S.

Iodine reacts with H_2SO_3 as follows:

$$I_2 + H_2SO_3 + H_2O = 2HI + H_2SO_4$$

and with $Na_2S_2O_3$ according to the reaction,

$$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6$$

we see therefore that one iodine is equivalent to ½ SO_2, ½ H_2SO_3 or ½ Na_2SO_3 and to one $Na_2S_2O_3$.

The latter reaction can be employed for the determination of copper as follows:

$$2Cu\ (C_2H_3O_2)_2 + 4KI = Cu_2I_2 + I_2 + 4KC_2H_3O_2$$

and taking the last two reactions we see that one molecule of $Na_2S_2O_3$ equivalent to one iodine is equivalent to one copper, so if we have a $^N/_{10}$ iodine solution we can use it to standardize a sodium thiosulphate solution and so indirectly determine copper by measuring the iodine liberated.

Suppose we have an iodine solution of unknown strength and a potassium dichromate solution whose strength is 1 c.c. = 0.0056 gram of iron. To find the strength of our iodine solution in terms of sulphur.

Make up a sodium thiosulphate solution of any convenient strength say 24.8 grams of the crystallized salt ($Na_2S_2O_3.\ 5H_2O$) per liter, approximately $^N/_{10}$.

Dissolve one gram of potassium iodide in water, acidify strongly with HCl and add 25 c.c. of the dichromate solution. Iodine will be liberated according to the reaction

$$K_2Cr_2O_7 + 6KI + 14HCl = 3I_2 + 8KCl + Cr_2Cl_6 + 7H_2O$$

or the amount of $K_2Cr_2O_7$ which oxidizes 6Fe liberates 6I; therefore the strength of the $K_2Cr_2O_7$ solution is 1.c.c. = 0.012685 gram of iodine and the weight of iodine liberated will be 25 × 0.012685 or 0.3171 gram.

Into this we run the sodium thiosulphate solution till it gives no blue color with starch; suppose this requires 25.5 c.c. then 1.c.c. = 0.01243 gram of iodine. Now take any convenient amount of the unknown iodine solution as 25 c.c. and titrate it with the sodium thiosulphate solution; suppose it requires 12.2 c.c. then its strength in terms of iodine is $\frac{12.2 \times 0.01243}{25}$ or 0.006058 and against sulphur when titrated as H_2S,

$$0.006058 : x :: 126.85 : 16.035$$

$$x \text{ or } 1 \text{ c.c.} = 0.000765 \text{ gram sulphur.}$$

Arsenic is determined by iodine according to the reaction:

$$Na_3AsO_3 + I_2 + 2NaHCO_3 =$$
$$Na_3AsO_4 + 2NaI + H_2O + 2CO_2$$

from which it is evident that 2I = 1As or 1 c.c. $^N/_{10}$ I = 0.003754 gram of arsenic or 0.00495 gram of As_4O_6. The available chlorine in bleaching powder can be determined according to a similar reaction by using a solution of Na_3AsO_3, which can conveniently be standardized by the $^N/_{10}$ iodine.

Antimony may be determined by sodium thiosulphate in a hydrochloric acid solution as follows:

$$SbCl_5 + 5KI = SbI_3 + I_2 + 5KCl$$
$$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6$$

Suppose we have a solution of $Na_2S_2O_3$ whose strength is 1 c.c. = 0.005 gram Cu. What is its strength in terms of antimony?

We see by comparing the reactions that 2Cu = I_2 and 1Sb = I_2 hence

0.005 : x : : 63.6 : 60.215. x = 0.00473 gram.

If the sodium thiosulphate were $^{N}/_{10}$ we should see at once its strength against copper and antimony, for one atom of copper brings into reaction one iodine equivalent to one half atom of oxygen or a $^{N}/_{10}$ solution of Cu = 6.36 grams per liter; while 1 Sb = 2I = 1 oxygen. So $^{N}/_{10}$ Sb = 120.43 ÷ (2 × 10) = 6.0215 grams and

1 c.c. $^{N}/_{10}$ $Na_2S_2O_3$ = 0.00636 gram Cu
= 0.00602 gram Sb.

ADJUSTMENT OF SOLUTIONS.

As this is in no sense a book on volumetric analysis a discussion of the merits of the different liters in practical use is out of place and the calculations are given so as to apply to whatever unit is taken for the volumetric apparatus.

Suppose we have made up ten liters of sulphuric acid approximately normal and find on standardizing that the strength is 1 c.c. = 0.050 gram H_2SO_4 and that in making the test we have used 50 c.c. of the solution. We have left 9,950 cubic centimeters and the solution is too strong. To find the amount of water to add to make it normal: let x be the volume required so that the solution shall be normal, then x times 0.049043 is the weight of H_2SO_4 contained therein ; $9{,}950 \times 0.050$ is the weight of H_2SO_4 in our solution. These quantities are equal as they will not be affected by dilution therefore we have

$$9{,}950 \times 0.050 = x \times 0.049043.$$

$x = 10{,}144.1$ c.c. So the amount of water to be added is $10{,}144.1 - 9{,}950$ or 194.1 c.c. (These cubic centimeters must accord with the liter adopted).

Suppose the solution gave on standardizing 1 c.c. = 0.048 gram H_2SO_4. The solution is too weak; by a similar method we can find the amount of water in excess and then add the proper quantity of sulphuric acid, we have

$$9950 \times 0.048 = x \times 0.049043. \quad x = 9738.4.$$

The excess of water is therefore $9950 - 9738.4$ or 216.6 c.c. For the amount of sulphuric acid to be added see Chapter VII.

It will be readily seen that it is much more convenient to make up the solutions too strong rather than too weak.

If we have a solution of say Na_2CO_3 which is too weak; find out the amount of water in excess, then calculate the amount of the salt for this volume of water and add it. The change in volume due to the solution of the salt can be neglected.

Example. A solution of Na_2CO_3 was found to have a strength 1 c.c. = 0.047 gram of H_2SO_4. How much Na_2CO_3 must be added to two liters to make it normal?

$$2000 \times 0.047 = x \times 0.049043. \quad x = 1{,}916.6.$$

There are 83.4 c.c. of water in excess. Now, a normal solution of Na_2CO_3 contains ½ molecular weight in grams per liter or 53.055 grams, so the amount to be added is

$$53.055 : y :: 1000 : 83.4. \quad y = 4.4244 \text{ grams}.$$

We may have two standard solutions of a reagent and desire to make a third of a certain intermediate strength — for example suppose we have two solutions of NH_4SCN

(a) 1 c.c. = 0.01275 gram of silver
(b) 1 c.c. = 0.00447 gram of silver

and we wish to make one liter of a solution equivalent to 10 mgs. of silver per c.c. How much of each shall we mix. Let x be the number of c.c. of (a); then 1000 − x = number of c.c. of (b): and we have

$$x\ (0.01275) + (1000 - x)\ 0.00447 = 10$$

(as one liter will contain 10 grams if 1 c.c. contains 10 mgs.) This gives 667.9 c.c. of (a) and 332.1 c.c. of (b).

If we have a solution of $KMnO_4$ containing 2 grams per liter and a $^N/_5$ solution of the same to make two liters of a $^N/_{10}$ $KMnO_4$. Let x be the volume of the 2 grams solution in liters and (2 − x) the volume of the $^N/_5$ solution; then $2\,x + (2 - x)\ 6.324 = 2\ (3.162)$ and $x = 1.4625$ liters, $(2 - x) = 0.5375$ liter.

SUBTRACTION OF EXCESS NECESSARY TO AFFECT THE INDICATOR.

In some titrations, conspicuously that of zinc by potassium ferrocyanide and that of lead by ammonium molybdate, the end point is not very sharp and a considerable excess of the standard solution is used before the indicator is affected. This amount should be determined by running a blank test under the same conditions as to temperature, bulk, acidity &c., and should be subtracted from the burette reading before calculating the results; for this amount is the excess necessary to affect the indicator and is required when there is no metal present. Other conditions remaining the same this excess is usually proportional to the bulk, but has to be determined for each set of conditions.

This subtraction of the excess necessary to turn the indicator can be omitted when the solution titrated contains nearly the same weight of metal, as well as the same volume &c., as was used in standardizing, for then this appears in the lower standard of the solution and no appreciable error is introduced. These conditions are however almost impossible to attain with a variety of ores, so that the best plan is to make the subtraction from every reading, for a color and set of conditions found satisfactory.

The following will illustrate this fact—

A solution of crystallized potassium ferrocyanide was made up for the titration of zinc ores, approximately, 44 grams per liter. To standardize; 200 mgs. of pure zinc were titrated under the standard conditions, using uranium acetate as an indicator. Then a blank was run under the same conditions.

0.200 gram of zinc + H_2O, HCl &c required 20.45 c.c.
Blank (H_2O, HCl &c) required 0.45 c.c.
0.200 gram of zinc required 20 c.c.
1 c.c. = 0.010 gram of zinc.

Disregarding the blank the strength becomes
1.c.c. = 0.00978 gram of zinc.

We now titrate one gram of an ore and use 21 c.c.: using the blank this gives 20.55%: disregarding the blank and using the lower standard gives 20.538%. Results close enough for ordinary work. But suppose we now titrate a rich ore, say one gram requires under the same conditions 56 c.c.: using the blank we get 55.55% and, disregarding the blank and using the lower standard, we get 54.768%. This involves an error not to be disregarded under any circumstances.

EXAMPLES.

1. Calculate the number of grams per liter to give normal solutions of oxalic acid, of tartaric acid, of acetic acid and of citric acid.

Ans. $H_2C_2O_4$, 45.01 grams; $H_2C_4H_4O_6$, 75.024 grams; $HC_2H_3O_2$, 60.032 grams; $H_3C_6H_5O_7$, 64.021 grams.

2. Calculate the number of grams per liter to give half normal solutions of I, of $Na_2S_2O_3$, $5H_2O$, and of SO_2.

Ans. I, 63.425 grams; $Na_2S_2O_3, 5H_2O$, 124.16 grams; SO_2, 16.017 grams.

3. Calculate the amounts necessary to make two liters of $^N/_{10}$ NaCl and NaBr.

Ans. NaCl 11.7 grams; NaBr 20.6.

4. Calculate the strength of $^N/_{20}$ $KMnO_4$ to be used in titrating $K_4Fe(CN)_6$.

Ans. 1.581 grams per liter.

5. What is the strength of $^N/_{10}$ $KMnO_4$ in terms of Fe? Fe_2O_3? Fe_3O_4? $FeSO_4, 7H_2O$?

Ans. 0.0056. 0.0080. 0.007735. 0.02782.

6. What is the strength of $^N/_{10}$ $KMnO_4$ in terms of $H_2C_2O_4$? of CaO? of $CaCO_3$? of $CaSO_4$?

Ans. 0.0045. 0.0028. 0.0050. 0.0068.

7. What is the strength of $^N/_{10}$ $KMnO_4$ in terms of P and of MoO_3 according to Noyes method?

Ans. 0.0000861 and 0.0048.

8. What is the strength of a $^{N}/_{10}$ sodium thiosulphate solution in terms of iodine? of copper?

Ans. 0.012685. 0.00636.

9. What is the strength of a $^{N}/_{5}$ iodine solution in terms of SO_2? H_2SO_3? Na_2SO_3?

Ans. 0.0064. 0.0082. 0.012616.

10. How many c.c. of $^{N}/_{5}$ $Na_2S_2O_3$ solution will be required to react with the iodine liberated by 20 c.c. of a $^{N}/_{10}$ $K_2Cr_2O_7$ solution? *Ans.* 10 c.c.

11. How many grams of copper will give when precipitated by potassium iodide sufficient iodine to require 20 c.c. of $^{N}/_{10}$ SO_2 solution? How many for 10 c.c. of $^{N}/_{10}$ $Na_2S_2O_3$ solution? *Ans.* 0.1272 and 0.0636.

12. Five grams of pig iron took 12 c.c. of $^{N}/_{100}$ iodine solution. What is the percentage of sulphur?

Ans. 0.0384%.

13. 1.5 grams of pig iron took 78 c.c. of $^{N}/_{10}$ $KMnO_4$. What is the percentage of phosphorus?

Ans. 0.447%.

14. In determining iron in an ore, by mistake too much $^{N}/_{10}$ $K_2Cr_2O_7$ was run in: the burette read 45 c.c.: 20 c.c. of $^{N}/_{10}$ $Fe_2(SO_4)_2$ were added and the titration finished: the burette then read 57 c.c. How much dichromate was required for the iron ore? *Ans.* 37 c.c.

15. Two liters of $KMnO_4$ solution were made up approximately $^{N}/_{5}$. It was found on standardizing that the strength was 1.c.c. = 0.01175 gram Fe and 48.2 c.c. were used. How much water must be added to what remains to make it $^{N}/_{5}$? *Ans.* 95.8 c.c.

16. How much NaOH must be added to 1.890 liters of NaOH solution, whose strength is 1 c.c. = 0.045 gram H_2SO_4, to make it normal? How much water to make it $^{N}/_{2}$?

Ans. 6.172 grams NaOH. 1581.3 c.c. water.

17. How many grams per liter of $KMnO_4$ will give a solution of such strength that 1 c.c. = 1% of iron when 0.50 gram is taken for analysis?

Ans. 2.8222 grams.

18. How many grams per liter of $K_2Cr_2O_7$ will give a solution of such strength that 1 c.c. = 1% of iron when 0.60 gram is taken for analysis?

Ans. 5.2570 grams.

19. How many grams of $Na_2S_2O_3$, $5H_2O$ per liter will give a solution such that 1 c.c. = 0.5% Cu, when one gram is taken for analysis?

Ans. 19.522 grams.

20. How much water must be added to two liters of $KMnO_4$, 1 c.c. = 0.0065 gram iron, to make it $^N/_{10}$?

Ans. 321.4 c.c.

21. How much water must be added to three liters of $K_4Fe(CN)_6$, 1 c.c. = 0.0115 gram zinc, to make it read percentage directly when one gram is taken for analysis? *Ans.* 450 c.c.

22. Given a solution of $K_2Cr_2O_7$, 1 c.c. = 0.0042 gram Fe, how many grams per liter of $KMnO_4$ will give a solution of equal strength?

Ans. 2.3715 grams.

23. One gram of an ore containing arsenic was treated according to Pearce's method and the arsenic precipitated as Ag_3AsO_4: the silver so combined was titrated by NH_4SCN. The amount used was 27.9 c.c. and the strength of the solution 1.c.c. = 0.007 gram of silver. What was the percentage of arsenic?

Ans. 4.52%.

24. A solution of $Na_2S_2O_3$ was made containing about 40 grams of the crystallized salt per liter; this was standardized by portions of copper 0.200 gram each;

they required 19.6 c.c. : 0.50 gram of a copper matte took 37.6 c.c. What is the percentage of copper?

Ans. 76.73%.

25. Given a solution of $KMnO_4$ 1 c.c. = 0.0056 gram of iron. What is its strength in terms of manganese by the Volhard method and by the Ford-Williams method?

Ans. { Volhard 1 c.c. = 0.00105 gram.
Ford-Williams 1 c.c. = 0.00275 gram.

26. The MnO_2 from one gram of spiegel was dissolved in 1.5 grams of ferrous ammonium sulphate, $(NH_4)_2SO_4$, $FeSO_4$, $6H_2O$, and then titrated by $^N/_{10}$ $KMnO_4$: 2.05 c.c. were used. What is the percentage of manganese? *Ans.* 9.94%.

27. In one gram of an antimony alloy, the antimony was determined by $^N/_{10}$ $Na_2S_2O_3$. 24.2 c.c. were required. What is the percentage of antimony?

Ans. 14.57%.

28. What amount of type metal must be taken for analysis so that the burette shall read percentage of antimony when $^N/_{10}$ $Na_2S_2O_3$ is used?

Ans. 0.602 gram.

29. Five grams of bleaching powder were mixed in a mortar with water and diluted to one liter: 50 c.c. of this required 30 c.c. of $^N/_{10}$ Na_3AsO_3 solution. What is the percentage of available chlorine?

Ans. 42.54%.

30. Under the conditions of the preceding example what fraction of normal will read percentage direct?

Ans. $\frac{N}{14.18}$

31. To 50 c.c. of a solution of chlorine an excess of potassium iodide was added; the liberated iodine was then estimated by a $^N/_{10}$ solution of $Na_2S_2O_3$ using starch

as an indicator; 22.5 c.c. of $Na_2S_2O_3$ solution were used. What is the strength of the chlorine solution?

Ans. 0.001595 gram per c.c.

32. Twenty grams of an adulterated sample of vinegar, freed from soluble sulphates, required 16 c.c. N NaOH: 10 grams gave 0.3162 gram of $BaSO_4$. What is the percentage of acetic acid? *Ans.* 3.176%.

33. 0.4 gram of impure caustic soda required when titrated directly 95 c.c. of $^N/_{10}$ HCl: another 0.4 gram was dissolved, an excess of barium chloride added, and then one-half titrated, requiring 46 c.c. What are the percentages of NaOH and Na_2CO_3?

Ans. $\begin{cases} \text{NaOH } 92.13\%. \\ Na_2CO_3\ 3.98\%. \end{cases}$

34. Two grams of impure potassium bicarbonate required when titrated cold, in a dilute solution, 6 c.c. of $^N/_{10}$ H_2SO_4: two grams when titrated boiling hot required 18 c.c. of N H_2SO_4. What are the percentages of K_2CO_3 and of $KHCO_3$?

Ans. 4.14% and 84.09%.

35. What volumes of $^N/_2$ and of $^N/_{10}$ H_2SO_4 must be mixed to give two liters of $^N/_5$ H_2SO_4?

Ans. ½ liter $^N/_2$ and 1½ liters $^N/_{10}$.

36. A $^N/_{10}$ iodine solution is 2% too strong. How many cubic centimeters of a $^N/_{100}$ iodine solution must be added to one liter to make it right?

Ans. 22.13 c.c.

37. Under certain conditions, in the titration of lead by ammonium molybdate, 0.75 c.c. was found necessary to turn the indicator: 0.300 gram of lead took 32 c.c. of the solution (without allowance). If the subtraction of the blank is omitted, what is the error in the titration of one gram of a 60% ore? *Ans.* 0.71%.

38. How much more N NaOH will it take to neutralize 1 gram of HCl than 1 gram HBr?

Ans. 15.08 c.c.

39. How much more N NaOH will it take to neutralize 1 gram of $NaHSO_4$ than N KOH to neutralize 1 gram of $KHSO_4$? *Ans.* 0.99 c.c.

40. 0.2 gram of a nitrogenous organic compound was heated with soda-lime and the NH_3 evolved caught in 50 c.c. $^N/_{10}$ HCl: the excess of HCl was neutralized by 14 c.c. of $^N/_5$ NaOH. What was the percentage of nitrogen? *Ans.* 15.44%.

CHAPTER VII.

CALCULATIONS OF DENSITY OF SOLIDS AND LIQUIDS.

DENSITY OF SOLIDS.

THE relative density or as it is commonly called specific gravity of solids and liquids is compared with that of water at the temperature of maximum density as unity. So if we say a substance has a specific gravity of 2.5, we mean that a given volume has 2.5 times the weight of the same volume of water at 4°C; or that its density relative to that of water is as 2.5 is to 1.

The density of solids can be determined by the following methods. The usual classification is given here but no formulae, as these are more confusing than helpful and do not lead to a thorough understanding of the subject.

A. Solids heavier than water and insoluble.

(1) Weigh in air and then in water.

According to the law of Archimedes, a body immersed in a fluid loses a part of its weight equal to that of the fluid it displaces. So the weight of the solid in air minus its weight in water gives the weight of an equal volume of water; as the volume of water displaced is equal to that of the object, unless it is porous, when it must be allowed to soak in water for some time to expel the air. So if we divide the weight in air by the loss in weight in water, we have the specific gravity or density compared to that of water at the temperature at which the experiment was carried out. This can then if necessary be corrected for the expansion of water and the true specific gravity compared to water at 4°C obtained. For great accuracy the weight in air should be reduced to weight in vacuo.

For example:— Suppose we have a piece of brass whose weight in air is 24.076 grams and in water 21.2436 grams. The weight in air divided by the loss in weight, 2.8324 grams, gives the specific gravity, 8.5, referred to that of water at the temperature of the experiment.

(2) If the substance is in small pieces or is a powder the following method is used:

(a) Weigh the substance in air.

(b) Weigh a small flask filled either entirely with water or to a certain mark.

(c) Place the substance in the flask, remove air, if necessary, by boiling and weigh with the water at the same point as before (either filled or to the mark).

It is evident that a volume of water equal to that of the substance has been displaced: to get the weight of this volume of water; weight of substance (a) + weight of flask and water (b) – weight of substance in flask and water (c) = weight of water displaced. Then weight of substance in air divided by the weight of an equal volume of water gives specific gravity. For example:

Weight of powder, 7 grams.

Weight of flask and water (to mark) 55 grams.

Weight of flask, powder and water (to mark) 59 grams.

We have $55 + 7 - 59 = 3$ weight of volume of water displaced by powder: and $\frac{7}{3} = 2.333$, the specific gravity of the powder.

By having graduations on the neck of the flask, the volume of the substance may be read off by the rise of the water in the flask, then this volume in c.c. multiplied by the weight of 1 c.c. of water at the temperature, gives the weight of an equal volume of water.

B. Solids lighter than water and insoluble.

As these solids are lighter, they cannot be weighed in water without a sinker.

The data necessary is—

Weight of substance in air.

Weight of sinker in water.

Weight of substance and sinker in water.

Or if we have the weight of sinker in air and its specific gravity we can calculate the weight of the sinker in water.

As the substance is lighter than water, the weight of sinker and substance in water is less than the sinker alone.

If we subtract from weight of sinker and substance in water the weight of sinker in water, we have the weight of substance in water, a negative quantity and the measure of its buoyant power.

Now the weight in air divided by the weight in air minus the weight in water is the specific gravity, but the weight in air minus the negative weight in water equals the weight in air plus the buoyant power, so we have in this case the specific gravity is equal to the weight in air divided by the weight in air plus the difference in weights of the sinker in water and the substance and sinker in water.

To illustrate by an example.—

Weight of substance in air 4 grams.

Weight of sinker in water 9 grams.

Weight of substance and sinker in water 8 grams.

Difference in weight of sinker in water and substance and sinker in water is one gram: weight in air plus this difference (or minus the negative loss in weight of one gram) is 5.

$\frac{4}{5} = 0.8$ the specific gravity of the substance.

If we have the weight of the sinker in air and its specific gravity.

The weight in air divided by the specific gravity gives the volume, or expressed in grams, the weight of an equal volume of water. This is equal to the loss of weight in water.

The weight in air minus the loss of weight in water gives the weight in water.

For example, suppose the sinker weighed 12 grams and its specific gravity was 8.

$\frac{12}{8} = 1.5$ (loss in weight) and $12 - 1.5$ or $10.5 =$ weight of sinker in water.

C Solids heavier than water but soluble.

Weigh in air then in a liquid of known specific gravity in which the substance is insoluble, such as turpentine, petroleum, alcohol, &c.

The weight in air divided by the loss in weight gives the density relative to the liquid used; suppose this is 7 and the specific gravity of the liquid 0.8, to find the specific gravity we have

$$7 : x :: 1 : 0.8 \text{ or } 7 \times 0.8 = 5.6 \text{ Sp. Gr.}$$

Or, the loss in weight of the solid equals the weight of liquid displaced. Let this be x and y the weight of the same volume of water; then $x : y :: 0.8 : 1$ and the weight in air divided by y gives the specific gravity.

To determine the specific gravity of rock salt. Given:
Weight of sample in air 10.436 grams
Weight of sample in turpentine 6.3547 grams
Specific gravity of turpentine 0.86

10.436 − 6.3547 = 4.0813 loss in weight in turpentine equal to the weight of an equal volume of turpentine.

Let y = weight of an equal volume of water

$$4.0813 : y :: 0.86 : 1. \quad y = 4.7457 \text{ and}$$

$$\frac{10.4360}{4.7457} = 2.199 \text{ Sp. Gr. of rock salt.}$$

or $\frac{10.436}{4.0813} = 2.5572$ density relative to turpentine and

$$2.5572 : x :: 1 : 0.86. \quad x = 2.199 \text{ Sp. Gr. of rock salt.}$$

D. Solid lighter than water and soluble.

Weigh with a sinker in some liquid which does not act on the substance and calculate the density relative to the liquid; then from the specific gravity of the liquid calculate the specific gravity as under C.

To determine the specific gravity of lithium—
Weight of lithium in air 3. grams
Weight of sinker in air 10. grams
Weight of lithium and sinker in kerosene 7.9222 grams.
Specific gravity of sinker (silver) 10.5
Specific gravity of kerosene used 0.829

First find the specific gravity of the sinker referred to kerosene

$$0.829 : 1 :: 10.50 : x. \quad x = 12.6658$$

Next find the weight of the sinker in kerosene we have

$$\frac{10}{10 - x} = 12.6658. \quad x = 9.2104$$

Now following the method for solids lighter than water and insoluble

$$\frac{3}{3 + 9.2104 - 7.9222} = 0.6996 \text{ density of lithium}$$

relative to kerosene: and to refer to water we have,

$$0.829 : 1 :: x : 0.6996. \quad x = 0.57996$$

The specific gravity of lithium is therefore 0.58.

In these examples no particular attention has been given to the temperature of the water, but the specific gravity has simply been referred to water at the same temperature (that of the experiment). To refer these specific gravities to water at 4°C; look up in the table, at the back of the book, the weight of a cubic centimeter of water at the particular temperature used, then substitute in the proportion,

Sp. Gr.x°C : Sp. Gr. 4°C : : 1 : wt. 1 c.c. water at x°C. *

This is the same proportion used for the conversion of the relative density of a solid in turpentine to density referred to water (specific gravity) and it is a similar proposition; for water at say 20°C is a liquid lighter than water at 4°C so the specific gravity referred to water at 4°C will necessarily be less.

The correction for the weight of the solid in air is too small to have significance here and will be discussed in the next chapter.

DENSITY OF LIQUIDS.

The specific gravity of liquids is determined as follows:

1st. By the pyknometer or specific gravity bottle.

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* The table also gives the volume of one gram of water at different temperatures. To use these values substitute in the proportion Sp. Gr. X°C : Sp. Gr. 4°C : : vol. at X°C : 1.

2d. By weighing a solid of known specific gravity in the liquid.

3d. By hydrometers.

4th. By Westphal's balance. This is really only a modification of the second method.

1st. In the pyknometer we can compare directly the weights of the same volume of the liquid and of water; so that the calculation only involves the subtraction of the weight of the pyknometer and the division of the weight of the liquid by that of an equal volume of water.

2d If we have, for example, a piece of brass, which weighs in air 10 grams, in water 8.824 grams and in the liquid of unknown specific gravity 9 grams: we have in each case the loss of weight of the brass equals the weight of the volume of liquid displaced; and, as the volume is the same in both cases, the loss in weight is directly proportional to the specific gravity and we have

1.176	:	1	::	1	:	x. $x = 0.85$
Loss of wt. in water.		Loss of wt. in Liquid.		Sp. Gr. of water.		Sp. Gr. of liquid.

Or if we know the weight of the brass in air and its specific gravity we can calculate the loss of weight in water as already explained under the density of solids.

3d Hydrometers are made either to read specific gravity direct, like the lactometer, or are graduated according to some arbitrary scale of degrees.

Degrees Beaumé and specific gravity may be compared by reference to the tables at the end of the book.

Degrees Twaddell have a direct relation to specific gravity. 200° represent the densities between 1 and 2 so 1° represents a difference of specific gravity of 0.005, hence the specific gravity is $1 + \frac{N° \text{ (Twaddell)}}{200}$.

.005
34
30
15
18

36° Twaddell is 1.18 Sp. Gr.
94° Twaddell is 1.47 Sp. Gr. and so on.

4th. In using the Westphal's balance each weight gives the figure for a decimal place beginning with the largest. If the liquid is heavier than water a weight (largest size) must be placed on the hook to help sink the float. This weight gives 1 (before the decimal point) and the remaining weights the decimals.

Under the specific gravity of liquids come the problems of dilution to a certain specific gravity. This can of course be done without any calculation by the use of a hydrometer. The following method will however be found useful, although not strictly accurate on account of a small contraction of volume on mixing which is found by very accurate measurements. *

Suppose we wish to make 200 c.c. of ammonia water 0.96 Sp. Gr. and we have, ammonia water 0.88 Sp. Gr. and water. The ratio is inversely as the difference in specific gravities .08 (.96 – .88) : .04 (1.00 – .96) : : volume of water : volume of ammonia: two parts of water to one of strong ammonia, or 66.66 c.c. diluted to 200.

Required to make six liters of nitric acid 1.26 Sp. Gr. having nitric acid 1.42 Sp. Gr. and water.

26 : 16 : : volume of acid : volume of water : or 16 parts of water for 42 of diluted acid : for 6 liters, 16 : 42 : : x : 6. $x = 2.285$. Or, let y = volume of nitric acid in liters $1.42\,y + 6 - y = 6\,(1.26)$. $y = 3.714$.

These methods can be applied to any case of mixing, as the contraction previously mentioned will not introduce any error appreciable in ordinary work.

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* See Wade, Journal Chemical Society p. 254, 1899.

Suppose we wish to make up two liters of a standard sulphuric acid solution containing ten grams of H_2SO_4 per liter. Dilute pure concentrated sulphuric acid with water to about 1.7 Sp. Gr. allow to cool to 15°C and then take the specific gravity most accurately, suppose it to be 1.689. The percentage of H_2SO_4 can be found by referring to a table* to be 76.29. The weight of sulphuric acid to be diluted will be $\frac{10 \times 2 \times 100}{76.29}$ = 26.2157 grams. This when diluted with water to two liters at 15° C will give a solution containing ten grams of H_2SO_4 per liter. In this calculation the specific gravity is referred to water at 15° C as unity, this is to agree with the liter used in dilution (volume of 1000 grams of water at 15° C). Should we wish to compare this with other specific gravities it can be reduced to specific gravity at 4° C as already explained.

This brings us to the consideration of changes in specific gravity due to temperature.

With solids the change in volume is so small that no appreciable error is introduced by neglecting this variation within the limits of laboratory temperature.

With liquids the variations of specific gravity due to changes in temperature are greater and cannot be disregarded. Unless specially stated the specific gravity is referred to water at 4° C as unity and for accurate work the determination must be carried out at that temperature. For many important solutions and liquids the corrections for temperature have been worked out and are to be found in the books on technical chemistry.

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* Marshall, J., Society Chemical Industry, vol. 18, p. 5, 1899.

Thorpe's Dictionary of Applied Chemistry gives the following variations of sulphuric acid

0° C	10° C	20° C	30° C	40° C	50° C
1.857	1.846	1.835	1.825	1.816	1.806

In many cases the correction is given for 1° C over a range of temperatures: these are added to the specific gravity at the temperature of the experiment to obtain the gravity at 4° C.*

VOLUME OCCUPIED BY PRECIPITATES.

In analyses such as that of pig lead for bismuth, the question of the volume occupied by a precipitate becomes of importance.

Suppose seventy-five grams of impure lead is dissolved in nitric acid, the lead precipitated by sulphuric acid, diluted to one liter and thoroughly mixed. To save time in filtering and washing, it is desired to draw off for the determination of bismuth, such a volume of the solution as shall represent fifty grams of the original sample.

Two-thirds of (1000 c.c. minus the volume of the precipitate) will be the volume required. The amount of impurities is small and the solubility of lead sulphate will not introduce an appreciable error, so we assume that the weight of lead sulphate will be proportional to the seventy-five grams of pig lead.

$$75 : x : : 206.92 : 302.99. \quad x = 109.82 \text{ grams}$$

The specific gravity of $PbSO_4$ is 6.2 therefore the volume occupied by the precipitate is $\frac{109.82}{6.2}$ or 17.7 c.c. So to

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* For a table of corrections for alcohol see Zeit. für Analytische Chemie, vol. 38, p. 253, 1899.

get a solution containing the bismuth from fifty grams of pig lead, we must draw off or filter through a dry filter $^2/_3$ (1000 — 17.7) or 654.86 c.c.

If we have a solution containing a precipitate and wish to titrate the excess of precipitant in a portion of the solution, we dilute to the mark in a flask, mix, and then draw off a portion with a pipette. Suppose the solution is diluted to 200 c.c. and 50 c.c. withdrawn; this is evidently more than one quarter on account of the volume occupied by the precipitate. This error is usually disregarded, but it can be found as follows. If we have precipitated the lead from one gram of lead ore as $PbCrO_4$, by a known amount of $K_2Cr_2O_7$, and wish to determine the excess by titration with potassium iodide and sodium thiosulphate in a portion of the filtrate; instead of filtering, washing and then diluting to a known volume we may proceed as follows: after adding $K_2Cr_2O_7$ in excess, dilute to 200 c.c. mix thoroughly and allow the precipitate to settle; then withdraw 50 c.c. of the clear solution and titrate the excess with sodium thiosulphate after adding potassium iodide and hydrochloric acid. This shows, we will assume, an excess of 100 mgs. of $K_2Cr_2O_7$; on the assumption that we have titrated one quarter of the solution, the total excess of $K_2Cr_2O_7$ will be 400 mgs. This is subtracted from the known weight of $K_2Cr_2O_7$ added and the lead present calculated from the remainder in the usual way, giving say 80% of lead.

Now that we have determined approximately the lead present, we can from this calculate the volume occupied by the lead chromate and so correct this percentage of lead for the volume occupied by the precipitate. 80% Pb = 0.8 gram Pb in one gram = 1.250 grams $PbCrO_4$.

The specific gravity of $PbCrO_4$ is 6, hence the volume occupied by the precipitate is $\frac{1.25}{6}$ or 0.21 c.c. 50 c.c. showed an excess of 100 mgs. of $K_2Cr_2O_7$, to get the correct total excess, we have— $50 : 200 - 0.21 :: 100 : x$. $x = 399.58$ mgs. or 0.42 milligram more $K_2Cr_2O_7$ was used in precipitating $PbCrO_4$ than was found before. Which is equivalent to 0.59 milligram of lead, so that the correct weight of lead present was 0.80059 gram, equivalent to 80.059%.

It will be observed that this correction depends mainly on two things—the excess of reagent and the dilution. If the excess is small and the dilution considerable, the error due to the volume of the precipitate can be neglected.

The accuracy of this method of calculating the volume of the precipitate is questioned by Ostwald, on account of the variation of the specific gravity of the precipitate in the solution, due mainly to adsorption. The method however is much used in commercial analytical work with satisfactory results.

EXAMPLES.

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1. A piece of barite (heavy spar) weighs in air 47 grams and in water 36.555 grams. What is its specific gravity? *Ans.* 4.5.

2. A specimen of magnetite weighed in air 27 grams and in water 21.60 grams. What is its specific gravity? *Ans.* 5.

3. A piece of loaf sugar weighed in air 7.5 grams and in petroleum ether, Sp. Gr. 0.645, 4.4635 grams. What is its specific gravity? *Ans.* 1.593.

4. A sample of magnetic sand weighed in air 12 grams. A flask filled with water to a mark weighed 47.5327 grams. The same flask containing the sand and filled to the same mark with water weighed 56.4281 grams. What is the specific gravity of the sand? *Ans.* 3.864.

5. To find the specific gravity of a piece of freshly cut pine wood. Given:

Weight in air, ...	10.100 grams
Weight of sinker in water, . .	12.24 grams
Weight of wood and sinker in water,	11.217 grams

Ans. 0.908.

6. To find the specific gravity of common salt, given the following data:

Weight of salt in air, . . .	8.8450 grams
Weight of flask and turpentine to mark,	45.2375 grams

Wt. of flask, salt and turpentine to mark,	50.5609 grams
Specific gravity of turpentine,	0.86

Ans. 2.16

7. To find the specific gravity of metallic sodium. Given:

Weight in dry air, ...	14.15629 grams
Weight in kerosene, ...	2.1807 grams
Specific gravity of kerosene, . . .	0.829

Ans. 0.98.

8. To find the specific gravity of turpentine. Given:

Weight of pyknometer, . . .	25.0456 grams
Wt. of pyknometer filled with water, .	72.1485 grams
Wt. of pyknometer filled with turpentine,	65.5541 grams

Ans. 0.86.

9. A piece of silver weighed 47 grams in water and 48.756 grams in petroleum ether, specific gravity 0.645. What is the specific gravity of the silver?

Ans. 10.5.

10. A ten gram brass weight, Sp. Gr. 8.5, weighed in glycerin 8.5135 grams. What is the specific gravity of glycerin? *Ans.* 1.2635.

11. Given the specific gravity of sulphuric acid as 1.84 compared to water at 15° C. What is its specific gravity compared to water at 4° C? (See tables.)

Ans. 1.8384.

12. Given the specific gravity of alcohol at 20° C referred to water at 4° C as 0.8332. What is its specific gravity referred to water at 20° C? *Ans.* 0.83467.

13. How much phosphoric acid, 1.7 Sp. Gr. and how much water are required to make 400 c.c. of 1.18 Sp. Gr.?

Ans. 102.85 c.c. phosphoric acid and 297.15 c.c. of water.

14. How much nitric acid 1.47 Sp. Gr. and water must be mixed to give three liters of 1.08 Sp. Gr.?

Ans. 510.6 c.c. nitric acid; 2489.4 c.c. water.

15. How much ammonia water 0.9 Sp. Gr. must be taken to make with water four liters 0.96 Sp. Gr.?

Ans. 1.6 liters.

16. We have two liters of dilute sulphuric acid 1.08 Sp. Gr., which we wish to use up in diluting concentrated sulphuric acid 1.82 to 1.20 Sp. Gr. How much concentrated acid is to be added? *Ans.* 387.1 c.c.

17 What is the volume occupied by 47 grams of $PbSO_4$. Sp. Gr. 6.2? *Ans.* 7.5 c.c.

18. How many c.c. of sulphuric acid, 1.824 Sp. Gr. compared to water at 15° C, weigh 100 grams?

Ans. 54.88 c.c.

19. What is the volume occupied by the barium sulphate from one gram of FeS_2? Sp. Gr. $BaSO_4$ 4.5.

Ans. 0.86 c.c.

20. To two grams of a mineral containing barium, 200 mgs. of $K_2Cr_2O_7$ were added to precipitate the barium and the solution diluted to 500 c.c., mixed and allowed to settle: 50 c.c. of the clear solution was titrated for the excess of $K_2Cr_2O_7$ by KI and $Na_2S_2O_3$ showing 4.2 mgs. What is the corrected percentage of barium oxide? Given the Sp. Gr. of $BaCrO_4$ as 3.9.

Ans. 8.2318%. Showing the correction to be insignificant.

CHAPTER VIII.

CALCULATIONS OF GASES.

Before proceeding to any of the calculations of gases or gas analysis a knowledge of the following laws is necessary.

Law of Boyle or Mariotte.

1. The temperature remaining the same, the volume of a given quantity of gas is inversely as the pressure it bears.

Law of Charles or Gay-Lussac.

2. The coefficient of expansion of all gases is 0.00366 or $\frac{1}{273}$ of the volume at 0° C.

Differently expressed, the volume of all gases is directly proportional to the temperature calculated from the absolute zero ($-273°$ C).

Law of Avogadro.

3. Under the same temperature and pressure equal volumes of all gases contain the same number of molecules.

It is evident from (1) and (2) that the volume of gases varies greatly under different conditions of temperature and pressure so that these must always be reduced to the standard conditions of 0° C and 760 millimeters pressure for comparison.

This is done as follows: Suppose we have six liters of a gas at 18° C. and 772 m.m. pressure and we wish to know the volume under the standard conditions. We can first correct for temperature and then for pressure or vice versa. The volume varies as the temperature calculated from the absolute zero, therefore

$$273 : 273 + 18 : : x : 6. \quad x = 5.6288.$$

The volume at 0° C and 772 m.m. is 5.6288 liters. The volume varies inversely as the pressure, therefore:

$$772 : 760 : : y : 5.6288. \quad y = 5.7176 \text{ liters,}$$

the volume of the gas at 0° C and 760 m.m. pressure.

These calculations are necessary in gas analysis and in many other analytical determinations where the volume of a gas is measured. When the gas is measured over water it contains aqueous vapor which supports part of the pressure: this tension increases with the temperature (see table), therefore before proceeding to the corrections for temperature and pressure as before, the tension of aqueous vapor must be subtracted from the barometer reading to get the real pressure supported by the gas. Take the following example of a nitrogen combustion. Weight substance 0.1923 gram: volume nitrogen 24.6 c.c.: temperature 25° C.: barometric pressure 771 m.m. The tension of aqueous vapor at 25° C is 23.5 m.m.; so 771 − 23.5 or 747.5 m.m. is the pressure supported by the nitrogen. As the volume varies inversely as the pressure, we have:

$$24.6 : x : : 760 : 747.5. \quad x = 23.93 \text{ c.c.}$$

(volume at normal pressure)

As volume varies directly as the temperature calculated from the absolute zero.

$$23.93 : y : : 273 + 25 : 273. \quad y = 21.95 \text{ c.c.}$$

volume of nitrogen at standard conditions. 1 c.c. nitrogen at 760 m.m. and 0° C weighs 0.001254 gram (see table).

Wt. of nitrogen is $0.001254 \times 21.95 = 0.02751$ gram and $\frac{0.0275}{0.1923} \times 100 = 14.31\%$ nitrogen.

Suppose we have 200 c.c. of gas at 10° C and 765 m.m. and wish to know the volume at 18° C and 772 m.m.: to correct for temperature, we have:

$$200 : x :: 273 + 10 : 273 + 18. \quad x = 202.08 \text{ c.c.}$$

and for pressure

$$202.08 : y :: 772 : 765. \quad y = 200.24 \text{ c.c.}$$

the volume under the desired conditions.

DENSITY OF GASES.

The density or specific gravity of gases is referred sometimes to air at 760 m.m. pressure and 0° C as unity and sometimes to hydrogen under the same conditions. In the actual determinations it is usually compared with an equal volume of air and then referred to hydrogen by calculation. Since a liter of hydrogen weighs 0.08952 gram under the standard conditions and a liter of air 1.29305 grams, the density referred to air can be referred to hydrogen by multiplying by 14.44 *

The important relation between the molecular weight and density of gases referred to hydrogen has already been mentioned under the calculation of atomic weights, as a means of determining what multiple of the equivalent is the atomic weight; it is also one of the most important methods for determining molecular weight. When

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* This factor is variously given from 14.438 to 14.443.

we say the density of a gas is 40 referred to hydrogen, it means that any given volume of the gas is 40 times as heavy as the same volume of hydrogen, under the same conditions of temperature and pressure. Now according to the law of Avogadro, these equal volumes of gases contain the same number of molecules so each molecule of the gas is 40 times as heavy as a molecule of hydrogen, and as the hydrogen molecule contains two atoms, a molecule of the gas is 80 times as heavy as a hydrogen atom or its molecular weight is 80. Or, in brief, the density of a gas (referred to hydrogen) is one half its molecular weight.

The exact calculation of density and so molecular weight varies with the method used, but in general it is as follows:

We have given the weight of a known volume of gas under certain conditions of temperature and pressure. Reduce these to 0°C and 760 m. m., and divide the weight by that of an equal volume of hydrogen and we have the density or specific gravity. The density of vapors is determined in a similar way, except that the volume occupied by the vapor from a known weight of substance, is measured instead of the weight of a known volume of vapor or gas. In many cases, especially when the heat necessary to convert the substance into the gaseous condition is high, it is more convenient to measure the volume of air displaced by the substance in the gaseous form, rather than the gas itself; but the calculation is the same, for the volume occupied by the air is the same as would be occupied by the vapor from the known weight of the substance at the same temperature and pressure.

The following determinations of the density of chloroform vapor by the three principal methods, illustrate these calculations.

(1) Dumas' method. Given the following data.—

Weight of bulb filled with air at 19°C and 763.9 m. m. = 36.4489 grams.

Weight of bulb filled with vapor at 101°C and 763.9 m. m. = 37.2085 grams.

Volume of air in the bulb at 19°C = 279 c.c.

First find the weight of the air contained in the bulb; by reducing the volume to the standard conditions and multiplying by 0.001293, the weight of 1 c.c. of air at 0°C and 760 m. m.

$$279 : x :: 273 + 19 : 273. \quad x = 260.8 \text{ c.c.}$$
$$260.8 : y :: 760 : 763.9. \quad y = 262.1 \text{ c.c.}$$

Weight of air is $262.1 \times 0.001293 = 0.3389$ gram.

Weight of bulb is $36.4489 - 0.3389 = 36.1100$ grams.

Weight of vapor is $37.2085 - 36.1100 = 1.0985$ grams

We now know that 279 c.c. of chloroform vapor at 101°C and 763.9 m. m. weighed 1.0985 grams.

To find the corresponding volume under the standard conditions, we have:

$$279 : x :: 273 + 101 : 273. \quad x = 203.8 \text{ c.c.}$$
$$203.8 : y :: 760 : 763.9. \quad y = 204.8 \text{ c.c.}$$

The weight of an equal volume of air will be 204.8×0.001293 or 0.2648 gram.

So $1.0985 \div 0.2648$ or 4.148 is the density referred to air: 4.148×14.44 or 59.897 is the density referred to hydrogen and 59.897×2 or 119.794 is the molecular weight. Theory 119.37.

(2.) Victor Meyer's method. Given the following data.

Weight of chloroform taken 0.2097 gram.

Volume of air expelled by vapor 43.65 c.c.

Temperature of air expelled 20°C.

Height of barometer 763.9 m. m.

Tension of aqueous vapor at 20°C (from table) 17.36 m. m.

We have the volume of air expelled by and equal to the volume of the vapor; to find its weight reduce this volume to the standard conditions;

$43.65 : x :: 273 + 20 : 273. \quad x = 40.67$ c.c.

$40.67 : y :: 760 : 763.9 - 17.36. \quad y = 38.50$ c.c.

$38.50 \times 0.001293 = 0.04978$ gram: weight of air.

Then $0.2097 \div 0.04978$ is 4.21, the density referred to air;

$4.21 \times 14.44 = 60.79$, the density referred to, hydrogen;

$60\ 79 \times 2 = 121.58$, the molecular weight.

(3.) Hofmann's method. The following data are required:

Weight of chloroform 0.1535 gram.

Volume of vapor at 100°C 79 c.c.

Height of barometer at 21°C 774.8 m. m.

Height of column of mercury (inside heating jacket) at 100°C 246.5 m. m.

Height of column of mercury (outside heating jacket) at 25°C 143.8 m. m.

* Tension of mercury vapor at 100°C 0.27 m. m.

This calculation involves, besides those already discussed, the reduction of the barometric readings to 0°C; because they are at such widely varying temperatures. The coefficient of the expansion of mercury is 0.00018

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* Ostwald Physico-chemical measurements p. 106.

for 1°C: so to reduce the reading representing the atmospheric pressure to zero, we have:

$$1 : 1 + (21 \times 0.00018) : : x : 774.8 \text{ or}$$
$$774.8 \div 1.00378 = 771.88 \text{ m. m.}$$

For the other columns of mercury we have:

$$246.5 \div 1.018 = 242.14 \text{ m. m. and } 143.8 \div 1.0045 = 143.15 \text{ m. m.}$$

The 79 c.c. of vapor is under the pressure indicated by the barometer minus the tension of mercury vapor (0.27 m. m.) and minus the sum of the two columns of mercury also supported by the atmospheric pressure (242.14 + 143.15). So the pressure is $771.88 - (0.27 + 242.14 + 143.15) = 385.56$ m. m.

We now know that 0.1535 gram of vapor at 100°C and 385.56 m. m. occupy 79 c.c. Reduce this as before to 0°C and 760 m. m. pressure and divide the weight by that of an equal volume of air:

$$79 : x : : 373 : 273. \quad x = 57.82 \text{ c c.}$$
$$57.82 : y : : 760 : 385.56. \quad y = 29.333 \text{ c.c.}$$
$$29.333 \times 0.001293 = 0.037927$$
$$0.1535 \div 0.037927 = 4.047$$

the density referred to air.

DENSITY BY EFFUSION.

The density or specific gravity of gases can be determined with sufficient accuracy for many practical purposes by the effusion test.*

This is based on the fact that the specific gravity of gases is proportional to the squares of the times of effusion. In these tests it is most convenient to determine

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* For details see Hempel's Gas Analysis, Dennis p. 212.

the specific gravity with reference to air and then, if necessary, refer it to hydrogen by calculation.

Suppose a certain volume of air requires twenty minutes to escape through an opening made by a needle in a platinum foil, and that under the same conditions of temperature and pressure the same volume of another gas requires twelve minutes.

Let x = density of this gas: then

x : 1 : : 144 : 400. x = 0.36, density referred to air, and 0.36 × 14.44 = 5.198, density referred to hydrogen.

This test is much used for illuminating gas at the works, but is not sufficiently accurate for scientific work.

CORRECTION OF WEIGHINGS.

According to the law of Archimedes, when any object is weighed under the ordinary conditions in air, we obtain less than the true weight on account of the loss in weight of the object equal to that of the air displaced. This correction is small, but it must be made in some cases, especially when large light apparatus is weighed, such as absorption bulbs &c., and in all very accurate determinations, such as atomic weights.

The correction is therefore the addition of the weight of an equal volume of air at the temperature of the weighing. This may be done as follows: weight in air then in water; the loss in weight is equal to the weight of the same volume of water; now, at the ordinary laboratory temperature the density of air referred to water as unity is 0.0012, so the loss in weight of the substance in water times 0.0012* is the correction to add.

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* This weight of 1 c.c. allows for mean humidity as well as temperature.

If the specific gravity of the object is known the correction can be calculated as follows:

$$\frac{\text{Wt. in air}^{*}}{\text{Sp. Gr.}} = \text{volume in c.c.}$$

Volume times weight of 1 c.c. of air (0.0012) is the correction to add.

In making corrections for weighing it must be borne in mind that we have:

(a) The apparent weight, that actually found.

(b) The true weight in vacuo, obtained by calculation.

To get the true weight of any object, we must add to its apparent weight the weight of an equal volume of air and subtract the weight of a volume of air equal to that of the weights used. The correction for the weights diminishes the correction for substances having a lower specific gravity than that of the weights; when the densities are the same the corrections equalize each other: when the density of the object is greater than that of the weights the correction becomes negative (is to be subtracted).

Suppose we have a 100 gram brass weight correct in air; it will weigh slightly more in vacuo. To find this weight we have:

$$\text{True weight} = \text{apparent weight} + \frac{(\text{true wt.} \times 0.0012)}{\text{Sp. Gr.}}$$

or $\frac{100}{8.5} \times 0.0012 = 0.0141$; so that the true weight in vacuo is 100.0141 grams.

Let us use this weight to weigh different substances and calculate their true weight.

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* The method given is all that is ever required but is not strictly accurate, for the true weight should be used instead of the weight in air.

1st. Sulphur, specific gravity 2. The correction will be volume × 0.0012 or $\frac{100}{2} \times 0.0012 = 0.06$ so that the true weight becomes

$$100 + (0.06 - 0.0141) = 100.0459.$$

We see from this that the true weight is that of the brass weight in air plus the weight of air displaced by the object less that displaced by the weight itself.

2nd. If we balance the 100 gram brass weight with brass of the same specific gravity, we shall have the correction to add $\frac{100}{8.5} \times 0.0012 = 0.014$ and that to deduct 0.014, so that the true weight coincides with the apparent weight.

3rd. If we balance the 100 gram brass weight with platinum, specific gravity 21.5, we shall find the true weight less than 100 grams; for the correction to add is $\frac{100}{21.5} \times 0.0012 = 0.0056$; while that to subtract is as before 0.014: hence the true weight becomes $100 + 0.0056 - 0.014 = 99.9916$ grams.

It will be seen from the preceding that the correction is different for brass and for platinum weights, and that the correction becomes greater as the specific gravity become less.

Suppose we have a glass vessel whose apparent weight is 75 grams when weighed with brass weights, and whose specific gravity is 2.5. What is the true weight?

The volume is $\frac{75}{2.5}$ or 30. c.c.; the weight of an equal volume of air is $30 \times 0.0012 = 0.036$ gram: the correction for the brass weights is $\frac{75}{8.5} \times 0.0012 = 0.0105$

gram: so the true weight becomes 75 + (0.036 − 0.0105) = 75.0255 grams.

The following table gives the weight in milligrams to be added or subtracted for each gram of apparent weight of substance, for different specific gravities, when weighed in air with brass weights.*

Sp. Gr.	Correction.	Sp. Gr.	Correction.	Sp. Gr.	Correction.
0.7	+ 1.57	2.0	+ 0.458	9.	— 0.009
0.8	+ 1.36	2.5	+ 0.337	10.	— 0.023
0.9	+ 1.19	3.0	+ 0.257	11.	— 0.034
1.0	+ 1.06	3.5	+ 0.200	12.	— 0.043
1.1	+ 0.95	4.0	+ 0.157	13.	— 0.050
1.2	+ 0.86	4.5	+ 0.142	14.	— 0.057
1.3	+ 0.78	5.0	+ 0.097	15.	— 0.063
1.4	+ 0.71	5.5	+ 0.075	16.	— 0.068
1.5	+ 0.66	6.0	+ 0.057	17.	— 0.072
1.6	+ 0.61	6.5	+ 0.042	18.	— 0.076
1.7	+ 0.56	7.0	+ 0.029	19.	— 0.080
1.8	+ 0.52	7.5	+ 0.017	20.	— 0.083
1.9	+ 0.49	8.0	+ 0.007		

CALCULATIONS OF GAS ANALYSIS.

With the help of the law of Avogadro we can very readily understand the combination of gases by volume. If we cause two liters of carbonic oxide to combine with one liter of oxygen, the product is not three liters of carbonic acid but two; for there are present the same number of molecules of CO_2 as there were of CO and as equal volumes of all gases contain the same number of molecules, an equal number of molecules occupy the

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* Calculated by Kohlrausch. Ostwald's Physico-Chemical Measurements.

same volume, at the same temperature and pressure: hence we have

$$2 \text{ vols. } CO + 1 \text{ vol. } O_2 = 2 \text{ vols. } CO_2.$$

This shows that the combination of the two gases is attended by a decrease in volume and that the resulting volume is two-thirds of that occupied by the mixture.

Similarly we have

$$2 \text{ vols. } H_2 + 1 \text{ vol. } O_2 = 2 \text{ vols. } H_2O \text{ (as steam)}$$

1 vol. $CH_4 + 2$ vols. $O_2 = 1$ vol. $CO_2 + 2$ vols. H_2O (as steam) or if the steam be allowed to condense

$$1 \text{ vol. } CH_4 + 2 \text{ vols. } O_2 = 1 \text{ vol. } CO_2 + \text{water.}$$

This law together with the corrections for temperature, pressure and tension of vapor, already explained, furnish all the information necessary to calculate gas analyses.

For example let us calculate the percentages from the following analytical results on a sample of water gas.

Volume taken for analysis, . . .	100 c.c.
Contraction due to absorption of CO_2, .	0.0 c.c.
" " " " " illuminants,	12.6 c.c.
" " " " " oxygen, .	0.9 c.c.
" " " " " CO, .	27.3 c.c.

We have left 59.2 c.c. of the original 100 c.c. containing hydrogen, methane &c., and nitrogen, 16.2 c c. of this are withdrawn to the explosion tube and mixed with 32.3 c.c. of oxygen and then diluted with 31.4 c.c. of air giving a total volume of 80.1 c.c.: this is then exploded and after allowing to cool the volume is found to be 53.4 c.c.

We have in the tube before explosion.

$$x \text{ Vols. } CH_4 + y \text{ vols. } H_2 + m \text{ vols. } N_2 + n \text{ vols. } O_2.$$

After explosion this becomes
x vols. CO_2 + (2 x + y) vols. H_2O (condensed) + m vols. N_2 (unaffected) + n − (2 x + ½ y) vols. O_2.

The volume of oxygen is diminished by a volume equal to twice that of the CH_4 plus one-half that of the hydrogen.

The CO_2 produced by the explosion is removed by dilute potassium hydroxide solution and the volume of the gas again measured = 45.8 c.c. The contraction in volume produced by the removal of CO_2 equals the volume of CH_4 present, 7.6 c.c. The contraction in volume due to the explosion, 26.7 c.c., therefore represents the volume occupied by the hydrogen (condensed to water) and the decrease of oxygen equal to twice the volume of CH_4 plus one half the volume of hydrogen. The CO_2 produced takes the place of the CH_4 originally present.

If we let x = vol. of hydrogen, we have:

$$26.7 = x + 2(7.6) + \tfrac{1}{2}x. \quad x = 7.66 \text{ c.c.}$$

Or, the volume of hydrogen = ⅔ of contraction minus twice the volume of CO_2 formed (second absorption by KOH).

As only a portion of the residual gas was taken for the explosion, the volumes obtained are referred to the original 100 c.c. by proportions:

for CH_4, 16.2 : 59.2 : : 7.6 : x. x = 27.77 c.c.
for H_2, 16.2 : 59.2 : : 7.66 : y. y = 27.99 c.c.

The results expressed in percentage by volume are: carbonic acid, none: illuminants, 12.6%: oxygen, 0.9%: carbonic oxide, 27.3%: hydrogen, 28%: methane &c., 27.7%: nitrogen (by difference) 3.5%.

For accurate work all volumes should be corrected for temperature, pressure, and vapor tension as already explained.

The following are results on coal gas with the Elliott apparatus:

Volume taken for analysis 100 c.c.

Reading after treatment with KOH. (CO_2) 0.0 c.c.

" " " " bromine (illuminants) 6.5 c.c.

Reading after treatment with alkaline pyrogallate (O_2) 7.4 c.c.

Reading after treatment with Cu_2Cl_2 and HCl (CO) 14.2 c.c.

Drawn off for combustion 15.8 c.c.

Volume after adding oxygen 48.0 c.c.

" " " air 79.7 c.c.

" " explosion 53.5 c.c.

" " washing with KOH 46.0 c.c.

The volume of $CH_4 = CO_2$ formed $= 53.5 - 46 = 7.5$ c.c.

As the volume of hydrogen $= \frac{2}{3}$ of contraction — twice the CO_2 formed: we have,

Volume of hydrogen $= \frac{2}{3}(26.2 - 15) = 7.46$ c.c.

To refer these quantities to the original 100 c.c. we have, residual volume $= 100 - 14.2$ c.c. $= 85.8$ c.c. and

for H_2, $15.8 : 85.8 :: 7.46 :: x$. $x = 40.5$

for CH_4, $15.8 : 85.8 :: 7.5 :: y$. $y = 40.7$

So our results become: carbonic acid, none: illuminants, 6.5%: oxygen, (7.4 − 6.5) 0.9%: carbonic oxide, (14.2 − 7.4) 6.8%: hydrogen, 40.5%: methane &c., 40.7%: nitrogen (by difference), 4.6%.

$\frac{PV}{T}$ 782

EXAMPLES.

1. Reduce twelve liters of oxygen, measured at 47°C and under a pressure of 782 m.m. of mercury, to the standard conditions. *Ans.* 10.5338 liters.

2. What will be the volume of nine liters of hydrogen (at the standard conditions) when heated to 120°C and under a pressure of 423 m.m.?

Ans. 23.278 liters.

3. Given 27 c.c. of nitrogen at 14°C and 752.1 m.m. What will be its volume at 20°C and 767.8 m.m.?

Ans. 27 c.c.

4. What is the weight of 77.2 c.c. of air measured over water at 27°C and 758 m.m. pressure? See tables. *Ans.* 0.08742 gram.

5. What is the weight of 17 liters of hydrogen, measured at 12°C and 3 atmospheres pressure? Take 1 atmosphere = 760 m.m of mercury.

Ans. 4.37342 grams.

6. What is the weight of 85 c.c. of NH_3 gas measured over mercury at 140°C and under a pressure of 770 m.m.? Given the tension of mercury vapor at 140°C = 1.76 m.m. *Ans.* 0.04324 gram.

7. Find the density referred to air of chloroform vapor. Given the following data for Dumas' method.

Weight of bulb and air at 20.5°C and 763.9 m.m. 34.8451 grams.

Weight of bulb and vapor at 116.5°C and 763.9 m.m. 35.8430 grams.

Volume of air in bulb at 20.5°C 394.93 c.c.

Ans. 4.10

8. What is the density referred to hydrogen of a substance which gave the following results by Victor Meyer's method?

Weight of substance taken 0.1307 gram.

Volume of air expelled (measured over water) 25.8 c.c.

Temperature of air expelled 20°C.

Height of barometer 763.9 m.m. *Ans.* 61.8.

9. What is the molecular weight of a substance which gave the following results by Hofmann's method.

Weight of substance used 0.1002 gram.

Volume of vapor 62.35 c.c.

Height of barometer at 21.5°C 771.5 m.m.

Height of column of mercury—(inside heating jacket) at 100°C 314 m.m.

Height of column of mercury—(outside heating jacket) at 26.5°C 135 m.m.

Tension of mercury vapor at 100°C 0.27 m.m.

Ans. 114.5.

10. What is the density referred to air of a gas, which escapes in 14.5 minutes through an opening, through which, at the same temperature and pressure, the same volume of air requires 19.5 minutes?

Ans. 0.55.

11. What is the density referred to hydrogen of a gas, which escapes in 7 minutes 30 seconds from an opening, while the same volume of air under the same conditions requires 5 minutes 10 seconds?

Ans. 30.44.

12. An object whose specific gravity is 3.38 (H_2O = 1.), weighed 39.7250 grams in air, when weighed with brass weights. What is its true weight?

Ans. 39.7335 grams.

13. An object whose specific gravity is 0.95 weighed 17.8540grams in air, when weighed with brass weights. What is its true weight? *Ans.* 17.8740 grams.

14. A bar of gold Sp. Gr. 19.3 weighed 10.73685 kilos, when weighed in air with brass weights. What is the true weight? *Ans.* 10.73600 Kilos.

15. A piece of pyrrhotite, Sp. Gr. 4.5, weighed in air 47.3854 grams, when weighed with platinum weights. What is its true weight? *Ans.* 47.3954 grams.

16. A piece of antimony, Sp. Gr. 6.8, weighed 75 grams in air; the weights used were 50 grams brass, 20 and 5 grams platinum. What is the true weight?

Ans. 75.0048.

17. If 50 c.c. of CH_4, 50 c.c. of H_2 and 50 c.c. of C_2H_4 were mixed with 450 c.c. of oxygen and exploded. What would be the resulting volume at the same temperature and pressure? (Assume that the temperature is below 100°C.). *Ans.* 325 c.c.

18. Calculate the percentage by volume of a blast furnace gas, giving the following results:

Taken for analysis 100 c.c.
Volume, after washing with KOH (CO_2) 99.4 c.c.
" " " " Br (illuminants) 99.4 c.c.
" " " " Alkaline "pyro" (O_2) 99.4 c.c.
" " " " Cu_2Cl_2, HCl (CO) 65.1 c.c.
Decrease in volume after explosion
(the whole used) 2.1 c.c.
Removed by washing with KOH none.

Ans. CO_2 0.6%. CO 34.3%. H_2 1.4%. N_2 63.7%.

19. Calculate the percentage by volume of a producer gas giving the following results:

Volume taken for analysis 100 c.c.
“ after washing with KOH (CO_2) 98.5 c.c.
“ “ “ “ Br (illuminants) 98.5 c.c.
“ “ “ “ Alk. “pyro.” (O_2) 98.5 c.c.
“ “ “ “ Cu_2Cl_2, HCl (CO) 75.0 c.c.

Decrease in volume after explosion, the whole used, 15 c.c. Removed by washing with KOH 3 c.c.

Ans. CO_2, 1.5%. CO, 23.5%. CH_4, 3%. H_2, 6%. N_2 by difference, 66%.

20. Calculate the composition of a coal gas given the following data:

Volume taken for analysis 100 c.c.
“ after washing with KOH (CO_2) 99.5 c.c.
“ “ “ “ Br (illuminants) 95.5 c.c.
“ “ “ “ Alk. “pyro.” (O_2) 95.0 c.c.
“ “ “ “ Cu_2Cl_2, HCl (CO) 89.0 c.c.

Decrease after explosion, one quarter used, 36.9 c.c.
Removed by washing with KOH 10.1 c.c.

Ans. CO_2, 0.5%. Illuminants (C_2H_4 &c.), 4%. O_2, 0.5%. CO, 6%. CH_4 &c., 40.4%. H_2, 44.5%. N_2, by difference, 4.1%.

CHAPTER IX.

CALCULATIONS OF CALORIFIC POWER.

Before taking up the calculations of the calorific power of the usual fuels, a few words on thermo-chemistry are necessary, to serve as an introduction to this and the following chapter. We have already discussed the qualitative and quantitative aspects of a chemical reaction; it remains to show here the thermo-chemical relations expressed.

All chemical reactions are accompanied by the liberation or absorption of a definite amount of energy, which may manifest itself in various ways, such as heat or electricity. Let us consider the equation:

$Zn + Cl_2 = ZnCl_2$, as written this signifies that 65.41 parts by weight of zinc combine with 70.9 parts of chlorine to give 136.31 parts of zinc chloride; but besides this, heat is liberated equivalent to 97,200 calories, when the quantities used are the atomic or molecular weights in grams, so

$$Zn + Cl_2 = ZnCl_2 + 97{,}200 \text{ calories.}$$

In other words 65.41 grams of zinc and 70.9 grams of chlorine contain when uncombined potential energy equivalent to 97,200 calories more tnan that of 136.31 grams of zinc chloride; consequently to decompose zinc chloride, into zinc and chlorine, energy must be expended, equivalent to that given up when combination took place or 97,200 calories per gram-molecule. This energy can be conveniently supplied in the form of an electric current; and the calculation of the voltage necessary to decompose certain molecules will be discussed in the next chapter.

The heats of formation of many molecules have been determined and are usually expressed in terms of heat developed by the formation of the molecular weight in grams of the substance; so that the numbers are directly comparable with the molecules taking part in reactions. This is not always the case however and care must be taken to ascertain whether the table is based on gram-molecules, gram-equivalents or grams of the compound formed.

The unit of heat is the calorie, the amount of heat necessary to raise one gram of water from 4° to 5° C.: as the specific heat of water does not vary greatly with the temperature, a calorie is taken practically as the amount of heat necessary to raise one gram of water one degree centigrade. Other units in use are: the greater calorie, the heat necessary to raise one kilogram of water 1° C, equal to 1000 calories: and a value denoted by K, introduced by Ostwald, the amount of heat necessary to raise one gram of water from 0° to 100° C, this is practically equal to 100 calories.*

The following are important thermo-chemical reactions:

$H_2 + O = H_2O + 68400$ calories (684 K)
$C + O = CO + 29000$ “ (290 K)
$CO + O = CO_2 + 68000$ “ (680 K)
$C + O_2 = CO_2 + 97000$ “ (970 K)
$S + O_2 = SO_2 + 71000$ “ (710 K)

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* A very full table of heats of formation expressed in terms of K will be found in Ostwald's Outlines of General Chemistry.

We see from these the amounts of heat given up by the formation of 18 grams of water, 28 grams of carbonic oxide etc. For the purpose of calculating the calorific power of fuel, it will be more convenient to have the amount of heat formed by the combustion of one gram of hydrogen, carbon and sulphur. If 2 + grams of hydrogen and 16 grams of oxygen give 18 + grams of water and 68,400 calories: one gram of hydrogen will give $\frac{68,400}{2}$ or 34,200 calories: similarly one gram of carbon $\frac{97000}{12}$ or 8083 calories and one gram of sulphur $\frac{71000}{32}$ = 2219 calories.

These heats of formation, so essential to the calculation of calorific power, are given various figures by different observers and it is a difficult matter to decide which to use. We shall adopt the following as having the greatest probability of accuracy and at the same time being in most general practical use.

One gram carbon to carbonic acid 8080 calories
One gram hydrogen to water (condensed) 34500 calories
One gram sulphur to sulphur dioxide 2220 calories

These numbers are the same in greater calories when one kilogram of the element is burned.

It will be seen from the preceding variations between the values of the fundamental data, that considerable uncertainty exists concerning thermo-chemical figures. The relative accuracy is much greater than the absolute; so the data employed should always be taken from the same source and if possible obtained by the same method.

With this introduction we proceed to the consideration of the calculations of the calorific power of fuel from a practical standpoint.

CALORIFIC POWER OF FUEL.

The calorific power of any solid fuel such as coal can be determined by three methods.

1st. By combustion in a calorimeter.

2nd. By calculation, from the results of an ultimate analysis.

3rd. By calculation, from the weight of lead reduced from litharge by fusion with a weighed quantity of the coal.

Only the first and second methods are applicable to liquids or gases.

1st. Of these three methods the first is the most accurate, as it affords a direct measure of the heating power of the fuel when burned under the most favorable conditions. The calculations involved do not specially belong to analytical chemistry, so the reader is referred to Poole on the Calorific Power of Fuels, for both a description of the apparatus and directions for the calculations.

2nd. The second method is largely used and is important for analysis, as they usually have the apparatus required to get the analytical results, while they are not often supplied with an expensive calorimeter.

For commercial purposes, calorific power is expressed in four ways:

1st. In calories per kilogram (greater calories), for example 7000 calories means that one kilogram of the fuel will raise the temperature of 7000 kilograms of water one degree centigrade.

2nd. In British thermal units (B.T.U.) or the amount of heat necessary to raise one pound of water one degree Fahrenheit.

3rd. In kilograms of water evaporated per kilogram of coal.

4th. In pounds of water evaporated per pound of coal.

The relations between these various ways of expressing calorific power are not complicated. To convert calories per kilogram into British thermal units it is only necessary to multiply by 1.8 for if a kilogram of coal heats 7000 kilograms of water one degree centigrade, one pound of coal will heat 7000 pounds of water one degree centigrade, and it only remains to multiply by the factor for converting centigrade to Fahrenheit degrees. Conversely to change B.T.U. to calories divide by 1.8 or multiply by $\frac{5}{9}$.

To find the number of kilograms of water evaporated by a kilogram of fuel, divide the calorific power (in calories per kilogram) by 536, the number of calories required to convert one kilogram of water at 100° C into steam at 100° C. If it should be necessary to raise the water from some temperature, for example 15° C to 100° C and then evaporate it: divide by $536 + (100 - 15)$ or 621. As the specific heat of water is taken as unity.

To find the number of pounds of water evaporated by a pound of fuel, divide the calorific power expressed in B.T.U. by 965 (536×1.8). For example, how many pounds of water will be heated from 59° F. to 212° F. and evaporated by one pound of a coal whose calorific power is 7000 (calories per kilogram)? $7000 \times 1.8 = 12{,}600$ B.T.U. It requires $212 - 59 = 153$ B.T.U. to heat a pound of water from 59° F. to 212° F. and 965 B.T.U. to convert it into steam at 212° F: So, $12600 \div (153 + 965) = 11.27$ pounds.

CALORIFIC POWER OF SOLIDS.

Given the composition of perfectly dry oak wood: carbon, 50.16%: hydrogen, 6.02%: oxygen, 43.36%: nitrogen, 0.09%: ash, 0.37%: to calculate its calorific power.

One kilogram will contain:

Carbon	501.6 grams	Nitrogen	0.9 grams
Hydrogen	60.2 "	Ash	3.7 "
Oxygen	433.6 "		

As part of the hydrogen is already in combination with oxygen, only the excess over the amount necessary to form water with all the oxygen is available as fuel: as 16 parts of oxygen combine with 2 of hydrogen, the hydrogen already in combination with oxygen will be 433.6 ÷ 8 = 54.2 grams: So we have available as fuel 6 grams of hydrogen and 501.6 grams of carbon.

0.006 kilogram hydrogen × 34500 = 207 calories
0.5016 " carbon × 8080 = 4053 "

Theoretical heating power = 4260 calories.

If the products of combustion escape at a temperature of or above 100°C., the heat given up by the condensation of the steam, which is lost, must be subtracted. This is found as follows: 60.2 grams of hydrogen give 9 × 60.2 = 541.8 grams of water; and as 536 calories are required to convert one kilogram of water at 100° to steam at 100°, the heat lost in this case will be equal to that required to change 541.8 grams of water into steam at 100°C or 536 × 0.5418 = 290 calories: so the available heat becomes 3970 calories. When the fuel has also hygroscopic moisture this must also be evaporated and if the products are not condensed, the heat necessary to do this must be deducted.

To calculate the calorific power of a coal whose composition is: carbon, 80.55%; hydrogen, 4.50%; sulphur, 0.54%; oxygen, (by difference) 2.70%; nitrogen, 1.08%; moisture, 2.92%; ash, 7.71%.

The nitrogen and ash are inert and simply diminish the available calorific power by the heat expended in bringing them to the temperature of the products of combustion, this amount is relatively very small and is neglected.

The moisture is objectionable as it must be raised to 100°C and then evaporated, thus rendering latent a portion of the heat evolved which can however be recovered if the products of combustion are cooled below 100°C.

The available hydrogen is calculated as before,

$$4.50 - \frac{2.70}{8} = 4.16\%.$$

One kilogram of the coal contains available as fuel:

41.6	grams	of hydrogen	giving	1435.2	calories
805.5	"	" carbon	"	6508.4	"
5.4	"	" sulphur	"	12.0	"
Theoretical calorific power =				7943.6	"

This on the basis of the condensation of the aqueous vapor produced which will then give up heat equal to that required to vaporize it, so no deduction is made. If the products are allowed to escape without condensation of the aqueous vapor, as is always the case in practice; the number of calories necessary to convert into vapor all the water present must be subtracted.

This will be, 9 × 4.5 (the percentage of hydrogen) = 405 grams per kilogram plus moisture 29.2 grams = 434.2 grams or 0.4342 kilogram; and 0.4342 × 536 (the number of calories necessary to convert one kilogram of water at 100°C to steam at 100°C) gives 232.7 calories. So under these conditions the available calorific power of the coal is 7710.9 calories. This can be corrected further for the heat necessary to raise the fuel to 100°C and for the heat lost by the escape of the products of combustion at temperatures above 100°C &c.

Taking 7711 as the calorific power of the coal, let us see the quantities of water it will evaporate.

Kilograms of water at 100°C per kilogram of coal

$$\text{will be } \frac{7711}{536} = 14.38.$$

Kilograms of water at 15°C per kilogram of coal

$$\text{will be } \frac{7711}{536 + (100 - 15)} = 12.41.$$

Pounds of water at 212°F. per pound of coal

$$\text{will be } \frac{7711 \times 1.8}{965} \text{ or } \frac{7711}{536} = 14.38.$$

Pounds of water at 40°F. per pound of coal

$$\text{will be } \frac{7711 \times 1.8}{965 + (212 - 40)} = 12.21.$$

This discussion can be summed up by the following formulae. Let x be the calorific power of the fuel, and let C, H, O, S and W be the weights of carbon, hydrogen, oxygen and hygroscopic water, expressed in kilograms: then we have,

$$x = 8080\,C + 34500\,(H - \frac{O}{8}) + 2220\,S.$$

An expression for the theoretical calorific power. And,

$$x = 8080\,C + 34500\,(H - \frac{O}{8}) + 2220\,S - 536(W + 9H)$$

For the available calorific power when the products of combustion are not condensed. The heat generated by the sulphur can usually be omitted without materially affecting the results.

Numerous formulae are given by different authorities, which differ somewhat from the preceding and attempt to bring the results by calculation nearer those obtained by the calorimeter, or the conditions of actual practice. Those given agree very closely with that of Dulong as recommended by the committee of the American Chemical Society.*

The reader is left to adapt them to particular conditions, with the caution not to trust too far to absolute figures obtained by calculation. The use of the method is to compare one fuel with another, in order to determine which is more economical, and for this purpose it is of value.

CALORIFIC POWER OF LIQUIDS.

These present no difficulties not already dicussed; for example, to calculate the theoretical calorific power of methyl alcohol, CH_3OH. We find the percentage composition to be: carbon, 37.46; hydrogen, 12.58; oxygen, 49.95: or expressed in kilograms C, 0.3746; H, 0.1258; O, 0.4995: the available hydrogen $(H - \frac{O}{8})$ is 0.0634 so we have

Hydrogen $0.0634 \times 34500 = 2187.3$ calories
Carbon $0.3746 \times 8080 = \underline{3026.7}$ calories
Theoretical calorific power 5214. calories

If the water formed is not condensed we must deduct $536 \times 9 \times 0.1258 = 607$ calories. Giving 4607 as the available calorific power.

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* J. Am. Chem. Soc. Dec. 1899.

The theoretical calorific power obtained by Stohmann is 5265 calories; this is a rather remarkable agreement as the calculated calorific power of liquids is not often reliable.

CALORIFIC POWER OF GASES.

In connection with the calorific power of gases some reasons can be shown for the discrepancy in results between the calculated and actual calorific power of solids and liquids. Let us consider the thermo-chemical reactions:

$$C + O_2 = CO_2 + 970\ K$$
$$2H_2 + O_2 = 2H_2O + 2(684)K$$
$$C + 2H_2 = CH_4 + 218\ K \text{ hence}$$
$$CH_4 + 2O_2 = CO_2 + 2H_2O + 2120\ K$$
$$2120 = 970 + 2(684) - 218,$$

or the heat produced by the combustion of 16 grams of CH_4 is 2120 K; less by 218 K than the heat produced by the burning of 12 grams of carbon and four grams of hydrogen.

In solids and liquids when we do not know the chemical compounds and only the ultimate composition we may be led into similar errors.

Sixteen grams of methane (CH_4) gave 2120 K hence one gram gives 132.5 K or 13250 calories and one kilogram the same number of greater calories. In the table at the back of this book, we find the weight of a liter of methane to be 0.71502 gram. The weight of a cubic meter is 1000 times this or an equal number of kilograms. The calorific power of a cubic meter will therefore be $13250 \times 0.715 = 9474$ calories (greater), and as a cubic meter = 35.3171 cubic feet, the calorific power per cubic foot is 268.2 calories. To convert this to B.T.U. per cubic foot it must be multipled by 3.97 giving 1065 as the calorific power of methane per cubic foot.

Now that we see the relation of these values we can conveniently use the following figures to calculate the theoretical calorific power of a gas per cubic foot measured at 0° C and 760 m.m. pressure

Hydrogen,	H_2	347.2	B.T.U per cubic foot.
Carbonic oxide	CO.	341.4	“ “ “ “
Methane	CH_4	1065	“ “ “ “
Illuminants	$C_2H_4 + C_3H_6$	2000	B.T.U. per cubic foot.

If we assume the initial temperature of the gas to be 60° F. and the products to escape at 328° F., without condensation, these figures become: *

Hydrogen	H_2	264.	B.T.U. per cubic foot
Carbonic oxide	CO	307.	“ “ “ “
Methane	CH_4	853.	“ “ “ “
Illuminants	$C_2H_4 + C_3H_6$	1700	“ “ “ “

Given a gas of the following composition, to calculate its theoretical calorific power in B.T.U. per cubic foot: hydrogen, 50.4%: methane, 33.7%: illuminants, 5.2%: carbonic acid, 2.6%: carbonic oxide, 5.8%: oxygen, 0.8%: nitrogen, 1.5%.

As all gases expand equally the percentage composition by volume is not affected by the temperature at which the analysis was made. In this case the oxygen cannot be in combination with the hydrogen, so we have available as fuel:

Hydrogen 0.504 Cu. ft. × 347.2 = 174.98 B.T.U.
Methane 0.337 “ × 1065. = 358.90 “
Illuminants 0.052 “ × 2000 = 104.00 “

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* For details of these calculations see Stillman's Engineering Chemistry, p. 263.

Carbonic oxide 0.058 Cu. ft. × 341.4 = 19.80 B.T.U.

Theoretical calorific power per Cu. ft. 657.68 B.T.U. To convert this to calories per cubic meter multiply by 8.896: which gives 5851.

The available calorific power, under the conditions stated, is found by using the values in the second table.

Many corrections might be added and other calculations, such as the volume of air required, the volume of the products of combustion, calorific intensity &c. Some of these can be done by the methods given under the calculations of gases, the others seem out of the sphere of analytical chemistry.

CALORIFIC POWER FROM WEIGHT OF LEAD REDUCED.

The method of calculating calorific power from the weight of lead reduced from litharge by a gram of the fuel is only suitable for coal or coke and is only valuable when the average weight of three lead buttons is multiplied by a factor proper for the fuel.

This factor should be obtained by comparison with the calorimeter and will be the calories developed by one gram divided by the lead reduced from litharge by one gram. When this is once obtained it will give satisfactory results with similar coals.

Berthier's idea that the calorific power was directly proportional to the oxygen consumed, *i. e.* the lead reduced, is disproved by the following:

$$C + 2\,PbO = 2\,Pb + CO_2$$

12 parts of carbon reduce 414 parts of lead hence,
1 kilogram of carbon reduces 34.5 kilograms of lead.
1 kilogram of carbon gives 8080 calories, hence,

the lead reduced times $\frac{8080}{34.5}$ or 234.2 gives the calorific power. The factor for hydrogen is obtained similarly:

$$H_2 + PbO = Pb + H_2O.$$

1 kilogram of hydrogen would reduce 103.5 kilograms of lead, and as one kilogram gives 34500 calories, the

$$\text{factor is } \frac{34500}{103.5} \text{ or } 333.33.$$

So it is evident that the more volatile matter, hydrocarbons &c., the coal contains, the higher must be the factor used.

When no better means of determining calorific power is available the weight of lead reduced by one gram times 240 for an anthracite or times 268.3* for a bituminous coal, will give approximately the calorific power.

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* Noyes J., Am. Chem. Soc. Vol. 17, 848.

EXAMPLES.

1. Find the theoretical calorific power of wood, whose composition is: carbon, 40%; hydrogen, 4.8%; oxygen, 33.8%; nitrogen, 0.4%; ash, 1%; hygroscopic water, 20%. Assuming the wood to be at 100°C and that the aqueous vapor is condensed.
Ans. 3430.4 calories.

2. Find the calorific power of peat, whose composition is: carbon, 39.3%; hydrogen, 3.9%; oxygen, 23.2 %; ash, 7.3%; water, 26.3%. Assuming that the products of combustion escape at 100°C. without condensation. *Ans.* 3191.3 calories.

3. Find the theoretical calorific power of a coal, whose composition is: carbon, 83.75%; hydrogen, 4.13 %; oxygen, 2.65%; nitrogen, 0.85%; sulphur, 0.57%; water, 0.80%; ash, 7.25%. *Ans.* 8090.6 calories.

4. In the preceding example, how many calories must be deducted if the aqueous vapor is not condensed?
Ans. 203.5.

5. Find the theoretical calorific power in B.T.U. of a coal whose composition is: carbon, 70.50%; hydrogen, 4.76%; oxygen, 15.71%; nitrogen, 1.36%; sulphur, 1.39%; ash, 6.28%. *Ans.* 12048.

6. How many kilograms of water at 20°C will be evaporated by one kilogram of a coal, whose calorific power is 13535 B.T.U.? *Ans.* 12.2

7. How many pounds of water at 25°C will be evaporated by a coal whose calorific power is 8000?

Ans. 13.1

8. How many kilograms of water at 60°C will be evaporated by a coal whose calorific power is 11270 B.T.U?

Ans. 10.86

9. What is the difference between the calculated available calorific powers of ethyl and methyl alcohol.

Ans. 2000 calories (in round numbers).

10. What is the calorific power of a natural gas, whose composition is: methane, 96.50%; illuminants, 1%; carbonic oxide, 0.5%; oxygen, 2%; in B.T.U. per cubic foot? Gas and products at 0°C.

Ans. 1049.

11. What is the calorific power of a coal gas, whose composition is: hydrogen, 50.4%; methane, 33.7%; illuminants, 5.2%; carbonic acid, 2.6%; carbonic oxide, 5.8%; oxygen, 0.8%; nitrogen, 1.5%; in B.T.U. per cubic foot? Assume that the gas enters at 60°F and the products of combustion escape at 328°F.

Ans. 527.

12. What is the calorific power of the following water gas: Hydrogen, 55%; methane, 5.75%; illuminants, 1.20%; carbonic acid, 4.05%; carbonic oxide, 31.00%; nitrogen, 3%; in calories per cubic meter? Gas and products at 0°C.

Ans 3398.

CHAPTER X.

ELECTRIC AND ELECTROLYTIC CALCULATIONS FOR DIRECT CURRENTS.

The calculations described in this chapter, although not essential to analytical chemistry, are added because electricity is so largely employed for both laboratory and industrial operations, and it is advisable that a chemist be able to make the ordinary calculations involved in its use. In order to make the description as concise as possible the subject is treated differently from the preceding chapters, and the important laws are expressed by formulæ, many of which are taken from an article by Prof. Crocker on the Theory of Electro-metallurgy.*

ELECTRIC CALCULATIONS.

The *ampere* is the unit of current, that is the rate of flow; it is the strength of current which when passed through a solution of silver nitrate in water, under certain standard conditions, will deposit silver at the rate of 0.001118 gram per second. Five amperes will deposit five times this amount *every* second. So to deposit 1.3416 grams of silver from an aqueous solution of silver nitrate in ten minutes requires two amperes; for

$$\frac{1.3416}{0.001118 \times 600} = 2.$$

The *coulomb* or ampere-second is the unit of quantity. It is the quantity of electricity which flows along a

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* School of Mines Quarterly. January, 1895.

conductor in one second when the current is one ampere. The total quantity or number of coulombs flowing in a given time is equal to the strength of current in amperes multiplied by the time in seconds or expressed in symbols

$$Q = Ct \qquad (1)$$

when Q = quantity in coulombs
C = strength of current in amperes
t = time in seconds

In dealing with large quantities of electricity the ampere-hour is used as a unit, an ampere flowing for an hour. This is 3600 coulombs.

If, for example, 1.5 amperes flow for 45 minutes the number of coulombs that have passed will be

$$1.5 \times 45 \times 60 = 4050 \text{ equal to } 1.125 \text{ ampere-hours.}$$

The *ohm* is the unit of resistance. It is the resistance offered to an unvarying electric current by a column of mercury at 0°C, one square millimeter in cross section and 106.3 centimeters long.

The resistance of a conductor, whether solid or liquid, to the passage of electricity has been found to depend upon its dimensions and the material of which it consists. For a given material it varies directly as the length and inversely as the area of the cross section.

The specific resistance of any material is the resistance measured between opposite faces of a cube of the material one square centimeter in area.

The resistance of any conductor is given by the formula,

$$R = \rho \frac{l}{a} \qquad (2)$$

in which

R is the resistance of the conductor in ohms
ρ is the specific resistance of the material in ohms
l is the length in centimeters, and
a is the area of the cross-section in square centimeters.

Therefore, if the specific resistance of a conductor is known the total resistance can be calculated from its dimensions. To find the resistance of 200 meters of German-silver wire having a cross section of 10 square millimeters; given the specific resistance of German-silver as 0.0000209.* Reduce the area to square centimeters and the length to centimeters and the resistance

$$\text{is } 0.0000209 \times \frac{20000}{10} = 4.18 \text{ ohms.}$$

Similarly, if a glass tube, 20 centimeters long with an internal cross section of 2 square centimeters, is filled with a solution of zinc sulphate whose specific resistance is 30 ohms, the total resistance will be

$$30 \times \frac{20}{2} = 300 \text{ ohms.}$$

The specific resistance is not absolutely constant but changes with the temperature. In the case of all metals it increases with the temperature while for carbon, selenium, liquids and solutions it diminishes as the temperature rises. For aqueous solutions it naturally varies with their strength.

Conductors are connected in series when the current passes through one after the other; in parallel, when they are connected side by side so as to furnish more than one path for the current. The total resistance of a number of separate resistances connected in series is

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* See Tables.

equal to their sum. If two paths of equal resistance are offered, the total resistance is only one half, as this is equivalent to doubling the cross section of the conductor, or the resistance of a number of equal resistances in parallel is equal to the resistance of one divided by the number so connected.

Conductance is the reciprocal of resistance, or the ease with which a current is allowed to pass. The total conductance of a number of separate conductances connected in parallel is equal to their sum. Thus five conductors each of 50 ohms resistance, connected in series give a resistance equal to their sum, 250 ohms; while connected in parallel they give the resistance of one divided by the number, 10 ohms. If three resistances of 20, 50 and 80 ohms respectively, are connected in series their total resistance is 150 ohms; while if connected in parallel their resistance is 12.12 ohms; for their respective conductances will be $\frac{1}{20}$, $\frac{1}{50}$ and $\frac{1}{80}$ and their total conductance the sum of the three, 0.0825. So that their total resistance is the reciprocal of 0.0825 or 12.12 ohms.

The *volt* is the unit of electromotive force or electrical pressure.

The relations between electromotive force, current, and resistance are expressed by Ohms Law; that the electromotive force acting between the extremities of any part of a circuit is the product of the strength of the current and the resistance of that part of the circuit, or

$$E = C\,R$$

or transposed $C = \frac{E}{R}$ (3)

To comply with Ohms Law and the definitions of the ampere and ohm the unit of electromotive force, the volt must be that electromotive force which steadily applied to a conductor whose resistance is one ohm will produce a current of one ampere.

The Clark cell at 15° C is the most constant source of electromotive force and is used as a standard. It gives an electromotive force of 1.434 volts.

Ohms law, equation (3) states that the amperes flowing in any circuit are equal to the volts divided by the ohms. This is the most important electrical law for by it when any two of the quantities involved are known the third may be determined. For instance if a conductor of 10 ohms resistance has flowing through it 3 amperes, the voltage measured between its ends must be $10 \times 3 = 30$ volts. Again if 18 volts are applied to the ends of a conductor of 9 ohms resistance the current will be $18 \div 9 = 2$ amperes. Finally if 0.1 of an ampere is desired from a source whose electromotive force is two volts, the total resistance of the circuit must be 20 ohms for as $E = C R$. $R = \frac{E}{C}$ and $2 \div 0.1 = 20$ ohms.

We are now in a position to consider the relations between electrical energy, heat and power.

Joule has shown by experiment that the relation between the heat developed in a circuit and the current flowing through it is expressed by the equation

$$V = C^2Rt \times 0.24 \qquad (4)$$

When

C is the current in amperes
R is the resistance in ohms
t is the time in seconds that the current has passed
V is the heat in calories.

Consequently 2 amperes passing through 5 ohms for 10 seconds develope

$$4 \times 5 \times 10 \times 0.24 = 48 \text{ calories.}$$

The constant 0.24 can be eliminated from equation (4) if instead of expressing the heat developed in calories we measure it in *joules:* for the *joule*, the electrical unit of heat, is 0.24 of a calorie.*

So if we designate the heat produced in joules by W the expression becomes

$$W = C^2Rt \tag{5}$$

and the heat developed by 2 amperes passing through 5 ohms for 10 seconds is $4 \times 5 \times 10 = 200$ joules.

Equation (5) may be written $W = C\,t + C\,R$. But we have already seen from equation (1) that $Q = C\,t$ and from Ohms law that $E = C\,R$; substituting these values we get:

$$W = Q\,E \tag{6}$$

This equation (6) shows that the heat, measured in joules, generated in a conductor is equal to the number of coulombs that have passed multiplied by the voltage between the ends of that conductor.

For example, if 1000 coulombs (10 amperes for one minute and forty seconds) have passed through a conductor, the voltage between whose ends is 10; there have been generated in that time 1000 joules, equal to 238.1† calories.

Since heat is a form of energy, the energy applied to the conductor expressed in joules is Q E. So that the

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* The latest determinations give one calorie equal to 4.2 joules which makes this constant 0.2381.

† From this point one calorie will be taken as 4.2 joules.

rate of work or power expressed in joules per second is $\frac{Q\,E}{t}$ or since $\frac{Q}{t} = C$ from equation (1) ; the power expressed in joules per second equals C E.

A joule per second is called a *watt* so if we designate the power expressed in watts by P we have

$$P = C\,E \qquad (7)$$

or the number of watts in any electrical circuit is equal to the product of the amperes and the volts. A circuit in which 4.2 amperes are flowing at a pressure of 100 volts is performing work at the rate of 420 watts, corresponding to 100 calories, per second.

The relations between the electrical and mechanical units of power are as follows:—

Rowland has shown that it requires 780 foot pounds of energy to heat one pound of water one degree Fahrenheit, or 3.1 foot-pounds to heat one gram of water one degree centigrade, one calorie. Since one calorie is equal to 4.2 joules, one foot-pound is equal to 1.356 joules or one joule equal to 0.737 foot-pound.

550 foot-pounds therefore equal 746 joules, and since 550 foot-pounds per second are one horse-power and a joule per second is a watt, 746 watts equal one horse-power.

The practical unit for measuring large quantities of electrical power is the kilowatt, one thousand watts. This is equal therefore to 737 foot-pounds per second or approximately 1⅓ horse-power.

ELECTROLYTIC CALCULATIONS.

When an electric current passes between platinum plates immersed in water acidified with sulphuric acid, water is decomposed, oxygen is liberated at the platinum anode and hydrogen at the platinum kathode: anode and kathode are the names given to the electrodes by which the current enters (anode) and leaves (kathode) the liquid. There is no liberation of hydrogen or oxygen except at the contact of the liquid with the electrodes. This chemical decomposition effected by the electric current is called *electrolysis* and the bath or material which undergoes decomposition the *electrolyte.*

Electrolytes may be solids, liquids or as recent experiments have shown, gases. Silver iodide is an example of a solid electrolyte, while as liquid electrolytes we have solutions of mineral salts and acids as well as many fused salts. An electrolyte must necessarily be a conductor of electricity and in the case of liquids be ionized. Liquids such as pure water, ether, and carbon bisulphide which are not perceptibly ionized are not considered electrolytes.

The constituents into which the electrolyte is split up by the current are called ions; that which is liberated at the anode is the anion, that which is liberated at the kathode the kathion. With very few exceptions an element or radical is always liberated at the same electrode. Ostwald* gives the following classification of ions—

KATHIONS.

Monovalent: H (in acids) K. Na. Li. Cs. Rb. Tl. Ag. NH_4. NH_3R to NR_4 (R being an organic radical) Cu (cuprous), Hg (mercurous).

Divalent: Ca. Sr. Ba. Mg. Fe (ferrous), Cu (cupric), Pb. Hg (mercuric), Co. Ni. Zn. Cd.

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* Scientific Foundations of Analytical Chemistry p. 53.

Trivalent: Al. Bi. Sb. Fe (ferric) and some of the rarer earth metals.

Tetravalent Sn (?). Zr.

ANIONS.

Monovalent: OH (in bases) F. Cl. Br. I. NO_3. ClO_3. ClO_4. BrO_4. MnO_4 (in permanganates) and the anions of all other monobasic acids the (acid molecule minus one hydrogen which goes to the kathode).

Divalent: S. Se. Te (?). SO_4. SeO_4. MnO_4 (in manganates), and the anions of dibasic acids.

Tri-to hexavalent: The anions of the tri-to hexavalent acids. Elementary anions with a valency of more than two are not known.

The quantity of the ions deposited by the passage of a current through an electrolyte was shown by Faraday to be very simply related to the quantity of electricity which passes.

Faraday's first law of electrolysis states: that the quantity of an electrolyte decomposed by the passage of a current of electricity is directly proportional to the quantity of electricity which passes through it. So as long as the quantity of electricity remains the same it is immaterial, so far as quantity deposited is concerned, whether the electricity passes as a very intense current for a short time or as a very weak current for a long time.

Faraday's second law of electrolysis states: that, if the same quantity of electricity passes through different electrolytes, the weights of the different ions liberated will be proportional to the chemical equivalents of the ions. Thus if the same current passes through a series of electrolytes from which it liberates as ions oxygen, hydrogen, silver, and chlorine, then for every 8 grams of oxygen evolved there will be liberated 1.008 grams of hydrogen 107.92 grams of silver and 35.45 grams of chlorine.

The electrochemical equivalent of a substance is the weight in grams deposited by the passage of one coulomb of electricity. Using this, Faraday's laws can be comprised in the statement: that the number of grams of an ion deposited during the passage of a current through an electrolyte is equal to the number of coulombs that have passed multiplied by the electrochemical equivalent of the ion. Since one ampere per second, from the definition of unit of current, deposits 0.001118 gram of silver and the chemical equivalent of silver is 107.92, the weight of any other element liberated by one ampere per second will be found by the proportion.

$$0.001118 : x : : 107.92 : A.$$

in which A is the chemical equivalent of the element, or

$$x = \frac{A\,(0.001118)}{107.92}$$

Therefore since $\frac{0.001118}{107.92} = 0.00001036$, the total weight deposited must be:

$$w = 0.00001036\ A\ C\ t. \qquad (8)$$

In which—

w is the weight in grams deposited.

A is the chemical equivalent, that is the atomic weight divided by the valency of the deposited ion

C is the current in amperes and

t is the time in seconds that the current flows.

Expressing the time in hours and denoting it by N, equation (8) becomes:

$$w = 0.0373 \text{ A C N.} \qquad (9)$$

C N being ampere-hours.

By transposing this equation, we get an expression for the amount of current required to deposit a given weight in a given time.

$$C = \frac{26.8 \text{ w}}{\text{A N}} \qquad (10)$$

and since from (7) the power in watts (P) is equal to the product of the amperes times the electromotive force (C E) we get

$$P = \frac{26.8 \text{ w E}}{\text{A N}} \qquad (11)$$

An expression for the power in watts necessary to deposit w grams of a metal whose chemical equivalent is A in N hours when an electromotive force E is used.

To illustrate the application of these formulæ:

The amount of oxygen liberated during the decomposition of acidulated water by a current of 2 amperes lasting 15 minutes is given by equation (8)

$$w = 0.00001036 \times 8 \times 2 \times 900 = 1.492 \text{ grams.}$$

The amount of copper deposited in 3 hours by a current of 25 amperes from a solution of copper sulphate is found by equation (9), to be

$$w = 0.0373 \times 31.8 \times 25 \times 3 = 8.895 \text{ grams.}$$

To determine the number of amperes that are necessary to deposit 500 grams of nickel in 5 hours, we employ formula (10) and find

$$C = \frac{26.8 \times 500}{29.35 \times 5} = 91.3 \text{ amperes.}$$

The power necessary to deposit 48.8 grams of zinc in four hours with a voltage of four is found by substitu-in equation (11), to be 40 watts.

$$P = \frac{26.8 \times 48.8 \times 4}{32.7 \times 4} = 40 \text{ watts.}$$

The fact that elements which form two series of salts have different electro-chemical equivalents according to the solution from which they are deposited, must be borne in mind when these calculations are made. For example copper forms two chlorides Cu_2Cl_2 and $CuCl_2$. In the former its chemical equivalent is twice its value in the latter: hence the actual weight of copper deposited is twice as great when a solution of cuprous chloride is electrolysed as with a solution of cupric chloride; the current and time being the same.

COUNTER-ELECTROMOTIVE FORCE.

When a molecule is formed by the combination of one or more elements, a definite amount of heat is evolved or absorbed. In most stable compounds heat is evolved: to decompose such a molecule energy must be supplied which is equivalent to this amount of heat. This energy can be supplied by an electric current. To separate metallic zinc from zinc sulphate requires energy to be given to the solution equivalent to the quantity of heat produced by the formation of zinc sulphate. Consequently when an electric current passes through an electrolyte, part of the electrical energy furnishes the energy necessary to overcome the chemical forces and only the remainder produces heat according to Joule's law. The electrolytic cell has therefore a counter-elecmotive force resisting the passage of or opposed to the current and the electromotive force producing that current.

Calling this counter-electromotive force e, the energy supplied must be a certain number of joules such that the electrical energy = Qe = Cet; depending upon the number of coulombs that have passed.
(Compare equation 6)

Or expressed in calories,

$$\text{Electrical Energy} = \frac{1}{4.2}\,\text{Cet}$$

Now the energy of combination of various compounds may be measured by the heat which is liberated when the combination takes place, that is

$$\text{Chemical Energy} = \text{w h},$$

when w is the weight of the element in grams and h is the number of calories produced when one gram of this metal combines with the other constituents of the compound.

Now from Faraday's law of electrolysis as given by equation (8) we have that w, the weight of metal deposited = 0.00001036 A C t, substituting this value for w, we have

$$\text{Chemical Energy} = 0.00001036\ \text{ACth} \qquad (12)$$

This chemical energy must equal the electrical energy supplied to the cell available for electrolysis, that is the electrical energy not producing heat.

Therefore

$$\frac{1}{4.2}\,\text{Cet} = 0.00001036\ \text{ACth}$$

which by cancelling Ct and reducing gives

$$\text{e} = 0.0000435\ \text{Ah} \qquad (13)$$

So the counter electromotive force is equal to the heat of combination of one gram in calories times the chemical equivalent times a constant, 0.0000435.

Instead of stating the heat of combination in terms of one gram of the metal, the more convenient method for electrolytic calculations is to state it in terms of the chemical equivalent in grams. For example, the chemical equivalent of zinc is 32.7 so that the heat of combination of 32.7 grams of zinc with other substances is the value to be used. When the values are given in terms of the molecular weight in grams these must be reduced to the heats of combination per equivalent by dividing by the valency or multiple of the valency of the element. The heat of formation of $Al_2(SO_4)_3$ is given by Thompson as 150630 calories: this means the combination of 54.22 grams of aluminium with sulphur and oxygen to give 342.43, the molecular weight in grams of aluminium sulphate. As the equivalent of aluminium is 9.037 we must divide by 6 (twice the valency as there are two atoms) to obtain the heat per equivalent, 25315 calories.

Calling the heat per chemical equivalent in grams H and remembering that A is the chemical equivalent and h is the heat evolved by the combination of one gram,

$$H = Ah,$$

substituting this value in equation (13) we get

$$e = 0.0000435\ H \text{ and}$$

since 0.0000435 equals $\frac{1}{22988}$. this equation reduces without appreciable error to the very simplest form of Thompson's law.

$$e = \frac{H}{23000} \qquad (14)$$

A definite case may make this deduction clearer. When 31.8 grams of copper, (the weight of the chemical equivalent in grams) combines to form copper sulphate, 27980 calories are developed. Now if no energy is lost as heat the electrical energy necessary to deposit 31.8

grams of copper from copper sulphate must equal this. This electrical energy is the product of e, the counter-electromotive force, and Q, the number of coulombs necessary to deposit 31.8 grams of copper. We find the number of coulombs by substituting in equation (8) giving

$$31.8 = 0.00001036 \times 31.8 \times Q$$

$$\text{or } Q = \frac{1}{0.00001036} = 96525 \text{ coulombs.}$$

Now as one calorie equals 4.2 electrical heat units we have

$$27980 \times 4.2 = e \times 96525$$

or $e = \frac{27980 \times 4.2}{96525}$ or practically $e = \frac{27980}{23000} = 1.22$ volts agreeing with formula (14) $e = \frac{H}{23000}$ where H is the heat produced by the combination of the chemical equivalent in grams expressed in calories.

This exceedingly simple formula* allows the electromotive force of any chemical reaction, whether it be direct as in a voltaic cell, or counter as in an electrolytic cell, to be easily calculated from the heats of combination. The calculated values agree in many cases very closely with those found by experiment. The discrepancies probably are due to the fact that all the energy of combination in the case of a voltaic cell, for instance, may not be converted into electrical energy, as some may be converted into heat which appears in the cell.

To calculate the voltage of a Daniel's cell: zinc is dissolved at one pole to form zinc sulphate, the electromotive

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* It is also applied to fused electrolytes. See Langley, J. Am. Chem. Soc., vol. 16, p. 52, 1894.

force is (14) $\frac{53045}{23000} = 2.31$ volts : at the other pole copper is deposited which sets up a counter-motive force found in the same way to be 1.22 volts. So that the available electromotive force of the cell (neglecting the slight electromotive force where the two solutions touch) is equal to $2.31 - 1.22$ or 1.09 volts. The electromotive force determined experimentally is about 1.08 volts. The table at the back of the book gives some of the most important values of H to be substituted in equation 14. If other tables are used, the different methods of expressing calorific power must be considered also in some cases the heat of solution and that of any chemical combinations which take place in the cell and so give energy which aids the current. For example when copper sulphate is decomposed in an aqueous solution we have:

Kathode $\leftarrow\!\!\circ$ Cu | $SO_4 \circ\!\!\rightarrow H_2SO_4 \leftarrow\!\!\circ H_2$ | O $\circ\!\!\rightarrow$ Anode.

We have in reality two decompositions and one combination so the electrical energy to be supplied is that equivalent to the heat of combination of $CuSO_4$ + its heat of solution in water + the heat of combination of H_2O − (the heat of combination of sulphuric acid + the heat developed on diluting with water).

When the heats of combination are taken from Ostwald's tables H is obtained as follows for copper sulphate and nickel sulphate

$CuSO_4$	1826K	$NiSO_4$aq.	2294K
Heat of solution	158K	H_2O	684K
H_2O	684K		2978K
	2668K	H_2SO_4aq.	2109K
H_2SO_4aq.	2109K		869K
	559K		

As these values are based on molecular weights in grams to be converted to equivalent weights they must each be divided by two, since copper and nickel are divalent ions; and since K = 100 calories we get,

$$\frac{279.5}{230} = 1.22 \text{ volts for } CuSO_4$$

and

$$\frac{434.5}{230} = 1.89 \text{ volts for } NiSO_4$$

The counter-electromotive force of any electrolytic cell can be easily determined experimentally as follows: Cause some deposition of the metal to take place by sending a current through the cell with a voltmeter connected between the electrodes. After a few moments, break the main circuit, and watch the voltmeter closely; the moment this occurs the needle will fall back to a certain point and stop there for an instant, then it will gradually drop down to zero. The point where the voltmeter needle stops first is the counter-electromotive force of the cell.

OHM'S LAW FOR ELECTROLYSIS.

In a circuit where electrolytic work is being done the quantities of electricity are not related in the form of Ohm's law already given (3) as the counter-electromotive force must be considered. The total electrical energy supplied to a circuit is given by equation (6) as equal to QE or CEt.

Similarly the chemical work done is Qe or Cet.

The heat generated is, from equation (5), C^2Rt. Now from the principle of conservation of energy we know that the electrical energy supplied must equal the sum of the heat produced and the chemical work done. Hence

$$CEt = C^2 Rt + Cet$$

Cancelling C and t we obtain

$$E = CR + e. \qquad (15)$$

Where E is the electromotive force required to produce the current C, e the counter-electromotive force of the electrolytic cell and R the total ohmic resistance in the circuit.

R may be separated into its constituent parts by calling Rg the resistance of the generator, Re the resistance of the conductors including any extra resistance inserted to regulate the current and Rc the resistance of the electrolytic cell: then equation (15) takes the form

$$E = C\ (Rg + Re + Rc) + e \qquad (16)$$

and solving for C we have

$$C = \frac{E - e}{Rg + Re + Rc} \qquad (17)$$

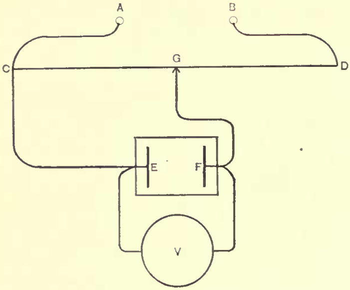
The effective electromotive force in the circuit is lower than the electromotive force of the generator by the counter-electromotive force of the electrolytic cell, so the current is equal to the difference of these electromotive forces divided by the total resistance. For any value of E smaller than e, no current will flow and no metal be deposited; so this counter-electromotive force is also the value which the applied electromotive force must exceed in order to produce decomposition.

This fact permits the deposition of a single metal from solutions containing several. For instance the heat of combination per equivalent of nickel sulphate in water is 43475 calories which means that it requires $\frac{43475}{23000} = 1.89$ volts to cause its decomposition and deposit nickel: to deposit copper from copper sulphate requires 1.22 volts. Therefore if we apply a voltage *above* 1.22 and *below* 1.89 to a cell containing a mixture of copper and nickel sulphate in solution only copper will be deposited. Given a solution containing silver and copper as nitrates. What are the limits of voltage to deposit silver and not copper? The heats of combination per equivalent of these salts in aqueous solution are respectfully 8390 and 26205 calories, dividing by 23000 we get the counter-electromotive force as 0.365 volt for silver nitrate and 1.14 volts for copper nitrate. So any current with a voltage above 0.365 and below 1.14 will deposit only silver from this solution.

When all of the first metal is deposited the current will fall to zero unless the voltage is raised above the counter-electromotive force of the next higher metal in solution.

A convenient method of regulating the voltage is shown by the diagram.

A and B are the poles of the source of current. The circuit is closed through a conductor CD whose resistance is sufficient to cut down the current. The resistance of this conductor must of course depend on the source of current, which may be either primary batteries, secondary batteries, dynamo or lightning circuit. The electrolytic cell is connected so that one pole E connects with C and the other pole F connects with the movable point or slider G so that any point of the conductor CD can be selected and any voltage from zero (when G is at C) to the full voltage of the source (when G is at D). By having a voltmeter V connected across the cell and starting with G at C the proper voltage can be applied by pushing G towards D until the voltmeter indicates the value desired.



The relation existing between the voltage measured across an electrolytic cell by a voltmeter and the current passing through the cell is given by equation (16); when Rg and Re are made zero, this becomes

$$E = CRc + e \qquad (18)$$

If Rc be negligible, then unless C is very great E = e, or the voltage across the cell is practically a constant, equal to the counter-electromotive force of the cell and independent of the current sent through it.

If either Rc or C is so great that e may be neglected then the voltage is proportional to the current flowing as in the case of simple conductor.

In most cases, however, neither can be neglected and the voltage across the cell depends not only on the counter-electromotive force but also on the resistance of, and the current flowing through the electrolytic cell. Let us consider an electrolytic cell containing a saturated solution of zinc sulphate with platinum electrodes 5 centimeters apart whose opposite submerged surfaces are 15 square centimeters, since the specific resistance is 33.7 ohms Rc in this case will be (equation (2)),

$$33.7 \times \frac{5}{15} = 11.23 \text{ ohms.}$$

The counter-electromotive force of zinc sulphate is 2.31 volts (see tables) if the current passing is one-tenth of an ampere, the voltage across the cell will be found by equation (18)

$$E = 0.1 \times 11.23 + 2.31 = 3.43 \text{ volts.}$$

If the current is raised to two-tenths of ampere the voltage will not be double, 6.86, but only 4.56 volts. For

$$E = 0.2 \times 11.23 + 2.31 = 4.56 \text{ volts.}$$

If the cell were so arranged that its internal resistance were only one-tenth of an ohm for small currents the voltage across its poles would be practically constant: for 0.05 of an ampere, 2.315 volts; for 0.10 of an ampere; 2.32 volts.

Silver nitrate in water requires only 0.365 of a volt to effect decomposition. Therefore, for such a cell, having a resistance of 100 ohms, with $^1/_4$ ampere passing through it, the voltage across the poles will be

$$E = {}^1/_4 \times 100 + 0.365 = 25.365.$$

When the current is doubled this becomes

$$E = {}^1/_2 \times 100 + 0.365 = 50.365.$$

or practically double.

EFFECT OF DISSOLVING ANODES.

In plating processes and the electrolytic refining of metals, the anode of the bath is made of the same metal as that to be deposited, so that as the current passes the anode dissolves at the same rate at which the metal is deposited on the kathode; keeping the solution at the same strength. A plating or refining bath, or any cell with a dissolving anode of the same metal as in the solution, has therefore no counter-electromotive force, since the electromotive forces of solution and decomposition are equal and opposed to each other.

Take the familiar example of a cell containing copper sulphate, the anode of platinum, the kathode of copper; this cell has a counter-electromotive force of 1.22 volts. When we substitute a copper anode for the platinum, no sulphuric acid is formed but the copper forms copper sulphate with the SO_4 and the anode dissolves at the same rate as the copper is deposited. The formation of copper sulphate ordinarily generates 27,980 calories per equivalent in grams, but here the energy appears as electricity and the electromotive force produced is exactly equal to that necessary to decompose copper sulphate. A bath or cell of this kind only introduces a certain ohmic resistance into the circuit (its e being zero) and for it formulæ 15, 16, 17, 18, reduce to the simplest form of Ohm's law. (3)

CURRENT DENSITY.

The character of the deposit depends largely on the strength of current used, which can only be determined by experiment. When this has been found, the current is often described as having a certain density, that is a certain number of amperes per unit of kathode area.

In analytical work current density is expressed in amperes per 100 square centimeters of kathode area; that is area on which metal is deposited. $N.D._{100}$ is the abbreviation used: so $N.D._{100}$ 0.25 means a quarter of an ampere for each 100 square centimeters of the submerged area of the kathode on which metal is deposited. As it is so important in this work to have a firm adherent deposit the current is most conveniently described by giving the voltage and current density. In some of the older books on the subject the current is given in cubic centimeters of mixed gases per minute, in order to reduce this to current density it is necessary to know that one ampere equals 10.436 c.c. of oxyhydrogen gas per minute measured at 0°C and 760 millimeters pressure.

EXAMPLES,

WITH SOLUTION OF EACH.

1. How many amperes are flowing in a circuit which in the course of one hour and 15 minutes has deposited 30.186 grams of silver? *Ans.* 6 amperes.

Solution. 1 hour and 15 minutes = 4500 seconds: one ampere by definition deposits 0.001118 gram of silver per second. Therefore in 4500 seconds it will deposit 0.001118 × 4500, or 5.031 grams. Number of amperes flowing equals 30.186 divided by 5.031 or 6.

2. If a current of 15 amperes flows for one hour and 20 minutes how many coulombs will pass? How many ampere-hours will that give?

Ans. 72000 coulombs, 20 ampere-hours.

Solution. Substitute in equation (1)

$Q = Ct = 15 \times 4800 = 72000$ coulombs: since 1 hr. and 20 minutes = 4800 seconds. 72000 coulombs ÷ 3600 = 20 ampere-hours.

3. If the specific resistance of copper is 0.000001629, what is the resistance of a wire 200 meters long having a cross-section of 2 square millimeters?

Ans. 1.629 ohms,

Solution. Substitute in equation (2) $R = \rho \frac{l}{a}$

$\rho = 0.000001629$, $l = 20000$ centimeters, $a = 0.02$ square centimeter.

$$R = 0.000001629 \frac{20000}{0.02} = 1.629.$$

4. If the specific resistance of German-silver is 0.0000209, what is the resistance of 150 meters of wire having a cross-section of 25 square millimeters.

Ans. 1.254 ohms.

Solution. Substitute in equation (2) $R = \rho \frac{l}{a}$

$\rho = 0.0000209$, $l = 15000$ centimeters, $a = 0.25$ square centimeter

$$R = 0.0000209 \frac{15000}{0.25} = 0.0000209 \times 60000 = 1.254$$

5. What is the resistance of an electric light carbon 12 inches long by $\frac{1}{4}$ inch in diameter when its specific resistance is 0.07. It will be sufficient to call $2\frac{1}{2}$ centimeters one inch.

Ans. 7 ohms.

Solution. Substitute in equation (2) $R = \rho \frac{l}{a}$

$\rho = 0.07$, $l = 12 \times 2.5 = 30$ centimeters, $a = \pi r^2 = \pi (\frac{1}{8} \times 2.5)^2 = 0.3$ very closely. $R = 0.07 \frac{30}{0.3} = 7$ ohms practically.

6. What is the resistance of a saturated solution of sulphate of copper placed in a tube 10 c.m. long and having a cross-section of 2 square centimeters, when its specific resistance is 29.3.

Ans. 146.5 ohms.

Solution. Substitute in equation (2) $R = \rho \frac{l}{a}$

$\rho = 29.3$, $l = 10$, $a = 2$. $R = 29.3 \frac{10}{2} = 146.5$

7. What is the total resistance in a circuit composed of a voltaic cell, a copper wire, an iron wire and a piece of German-silver all connected in series when the separate resistances are respectively 3, 2, 4, 6?

Ans. 15 ohms.

Solution. Total resistance of resistances connected in series equals their sum.

8. What is the resistance of eleven incandescent lamps connected in parallel if each has a resistance of 220 ohms when hot. *Ans.* 20 ohms.

Solution. Resistance of equal resistance connected in parallel is equal to resistance of one divided by their number.

9. What is the resistance of four wires of respectively 20, 5, 4, and 2 ohms connected in parallel.

Ans. One ohm.

Conductance of a number of conductances connected in parallel equals their sum. $\frac{1}{20}, \frac{1}{5}, \frac{1}{4}, \frac{1}{2}$ equals $.05 + .2 + .25 + .50 = 1$. Reciprocal of one is one.

10. If 6 amperes are flowing through 7 ohms, what is the voltage measured between the ends of this resistance?

Ans. 42 volts.

Solution. Ohm's law, $E = CR = 6 \times 7 = 42$.

11. If a voltage of 17 is applied to 34 ohms how many amperes will pass? *Ans.* 0.5 ampere.

Solution. $C = \frac{E}{R} = \frac{17}{34} = 0.5$

12 What is the resistance of a conductor that allows $\frac{3}{4}$ of an ampere to flow when a voltage of 75 is applied to its terminals? *Ans.* 100 ohms.

Solution. From Ohm's Law $R = \frac{E}{C} = \frac{75}{0.75} = 100$

13. If a wire of 2 ohms resistance is immersed in 100 grams of distilled water how long will it take $\frac{3}{4}$ of an ampere to raise the temperature of the water from 4 to 6 degrees centigrade, assuming no loss from radiation. *Ans.* 12 minutes 21 seconds.

Solution. 100 grams of water raised 2° = 200 calories. Substitute in formula (4)

$V = C^2Rt \times 0.24$. $V = 200$, $C = {}^3/_4$, $R = 2$.

$$200 = \frac{9}{16} \times 2 \times t \times 0.24 = 0.27\,t. \qquad t = 741 \text{ seconds}$$

or 12 minutes 21 seconds.

14. How many joules would be expended as heat by 3 amperes flowing through 2 ohms for 10 minutes.

Ans. 10,800 joules.

Solution. Substitute in equation (5) $W = C^2Rt$.

$C = 3$, $R = 2$, $t = 600$. $W = 9 \times 2 \times 600 = 10800$.

15. An enclosed arc lamp requires 5 amperes to burn properly. When placed on an 118 volt circuit, how many watts are taken? *Ans.* 590 watts.

Solution. Substitute in equation (7)

$P = CE$ $C = 5$, $E = 118$. $P = 5 \times 118 = 590$.

16. How many watts do 25 incandescent lamps take connected in parallel from a 110 volt circuit, when each lamp draws half an ampere? How many kilowatts and how many horse-power does this make? *Ans.* 1375 watts, 1.375 kilowatts and 1.84 horse-power.

Solution. 25 lamps at ${}^1/_2$ ampere apiece gives 12.5 amperes. Substitute in equation (7) $P = CE$,

$C = 12.5$, $E = 110$, $P = 12.5 \times 110 = 1375$.

1000 watts = 1 kilowatt. 1375 watts = 1.375 kilowatts.

746 watts = 1 horse-power. 1375 watts = 1.84 horse-power.

17. At full load a dynamo delivers 600 amperes at 125 volts what is its output in watts and what would be its rating in kilowatts and horse-power.

Ans. 75000 watts, 75 kilowatts, 100 horse-power.

Solution. Substitute in equation (7)

$P = CE$. $C = 600$, $E = 125$, $P = 75000$.

$\frac{75000}{1000} = 75$ kilowatts, 1 kilowatt $= 1\ ^1/_3$ horse-power, $75 \times 1\ ^1/_3 = 100$ horse-power.

18. How much zinc will be deposited from zinc sulphate by 3 amperes in 10 minutes? *Ans.* 0.6098 gram.

Solution. Substitute in equation (8)

$w = 0.00001036$ ACt. $A = 32.7$, $C = 3$, $t = 600$. $w = 0.00001036 \times 32.7 \times 3 \times 600 = 0.0003388 \times 1800 = 0.6098$ gram.

19. How much lead will be deposited by a current of $^1/_2$ an ampere passing for 90 minutes through lead chloride. *Ans.* 2.894 grams.

Solution. Substitute in equation (8)

$w = 0.00001036$ ACt $A = 103.5$, C $^1/_2$, $t = 5400$.

$w = 0.00001036 \times 103.5 \times {}^1/_2 \times 5400$

$= 0.001072 \times 2700 = 2.894$ grams.

20. How much chlorine would be liberated by $^1/_2$ an ampere passing through dilute hydrochloric acid for 13 hours. *Ans.* 8.593 grams.

Solution. Substitute in equation (9)

$w = 0.0373$ ACN. $A = 35.45$, $C = {}^1/_2$, $N = 13$.

$w = 0.0373 \times 35.45 \times {}^1/_2 \times 13$

$= 1.322 \times 6.5 = 8.593$ grams.

21 How much tin will be deposited by 5 amperes flowing 6 hours through a solution of $SnCl_2$?

Ans. 66.6 grams.

Solutiun. Substitute in equation (9)

$w = 0.0373$ ACN. $A = 59.52$, $C = 5$, $N = 6$

$w = 0.0373 \times 59.52 \times 5 \times 6$

$w = 2.220 \times 30 = 66.6$ grams.

22. How many amperes will it take to deposit 2½ pounds of copper from copper sulphate in 10 hours?

Ans. 95.7 amperes.

Solution. Substitute in equation (10)

$C = \frac{26.8\ w}{AN}$. w = 1136 grams. 1 kilo = 2.2 lbs. hence 2.5 lbs = 1.136 kilos = 1136 grams.

$$A = 31.8,\ N = 10. \quad C = \frac{26.8 \times 1136}{31.8 \times 10} = 95.7 \text{ amperes.}$$

23. What is the minimum voltage necessary to decompose water if the heat of combination of one gram of hydrogen with oxygen is 34180 calories.

Ans. 1.486 volts.

Solution. Substitute in equation (14)

$$e = \frac{H}{23000} = \frac{34180}{23000} = 1.486 \text{ volts.}$$

24. If zinc bromide requires 1.65 volts to decompose it, what is the heat evolved by the equivalent weight of zinc in grams combining with bromine?

Ans. 37950 calories.

Solution. From equation (14) H = 23000 e hence $H = 23000 \times 1.65 = 37950$.

25. If one gram of hydrogen combining with chlorine in the presence of water evolves 39315 calories what is the voltage required for the decomposition of hydrochloric acid? *Ans.* 1.71 volts.

Solution. Substitute in equation (14)

$$e = \frac{H}{23000} = \frac{39315}{23000} = 1.71 \text{ volts.}$$

26. It is desired to send half an ampere through ten ohms of copper sulphate. What resistance must be put in series with the cell if the current is to be drawn from a circuit whose voltage is 118. What will be the values of this extra resistance for respectively ¼ and 2 amperes? *Ans.* 223.56, 457.12, and 48.39 ohms.

Solution. Neglecting the resistance of the generator and leads equation (16) becomes for this example:

$E = C(R_1 + R_c) + e$. $E = 118$, $C = 1/2$, $R_c = 10$, $e = 1.22$

$118 = 1/2(R_1 + 10) + 1.22$

$1/2 R_1 = 118 - 5 - 1.22 = 111.78$ $R_1 = 223.56$ ohms.

If $C = 1/4$. $118 = 1/4(R_1 + 10) + 1.22$

$1/4 R_1 = 118 - 2.5 - 1.22 = 114.28$ $R_1 = 457.12$ ohms

If $C = 2$. $118 = 2(R_1 + 10) + 1.22$

$2R_1 = 118 - 20 - 1.22 = 96.78$. $R_1 = 48.39$ ohms.

27. Two batteries, having a negligible internal resistance and a voltage of two each, are to furnish current to be sent through a solution of zinc sulphate of 2.7 ohms resistance. What extra resistance must be inserted to limit the current to half an ampere? How much more must be added to cut the current down to 1/4 of an ampere?

Ans. 0.68 of an ohm, 3.38 ohms additional.

Solution. Substitute in $E = C(R_1 + R_c) + e$

$E = 4.$, $C = 1/2$, $R_c = 2.7$, $e = 2.31$ (see tables)

$4 = 1/2(R_1 + 2.7) + 2.31$. $1/2 R_1 = 4 - 1.35 - 2.31$.

$1/2 R_1 = 0.34$. $R_1 = 0.68$ of an ohm.

If $C = 1/4$, $4 = 1/4(R_1 + 2.7) + 2.31$. $1/4 R_1 = 4 - 0.675 - 2.31 = 1.015$. $R_1 = 4.06$. $4.06 - 0.68 = 3.38$ ohms additional.

28. What current will pass through a tube of acidulated water, having a resistance of 25 ohms, between platinum electrodes when connected to a 118 volt circuit in series with 6 lamps in parallel assuming each lamp to be 240 ohms resistance. What will be the value of the current when half the lamps are unscrewed?

Ans. 1.79 and 1.11 amperes.

Solution. Substitute in equation (17)

$E = 118$, $e = 1.486$ example (23) $R_g = 0$, neglected, $R_1 = \frac{240}{6} = 40$, $R_c = 25$.

$$C = \frac{118 - 1.486}{40 + 25} = \frac{116.514}{65} = 1.79 \text{ amperes.}$$

For 3 lamps $R_1 = \frac{240}{3} = 80$. $C = \frac{118 - 1.486}{80 + 25} = \frac{116.514}{105}$ $= 1.11$ amperes

29. What is the voltage across an electrolytic cell of silver nitrate having a resistance of 40 ohms when half an ampere is passing. *Ans.* 20.365 volts.

Solution. Substitute in equation (18) $E = CR_c + e$. $C = \frac{1}{2}$, $R_c = 40$, $e = 0.365$ (see tables) $E = \frac{1}{2} \times 40 + 0.365 = 20.365$ volts.

30. What is the voltage across an electrolytic cell of zinc bromide of 2 ohms resistance when the circuit is closed by inserting $1\frac{1}{2}$ ohms from a storage battery giving 4 volts. *Ans.* 3 volts practically.

Solution. First find C from equation (17) $C = \frac{E - e}{R_1 + R_c}$. $E = 4$, $e = 1.65$ (example 24) $R_1 = 1.5$ $R_c = 2$.

$$C = \frac{4 - 1.65}{1.5 + 2} = \frac{2.35}{3.5} = 0.67 \text{ practically}$$

Now substitute in equation (18) $E = 0.67 \times 2 + 1.65 = 1.34 + 1.65 = 2.99$ volts, practically 3.

TABLES.

TABLES OF WEIGHTS.

METRIC SYSTEM.

Milligram = 0.015438395 grains.
Gram = 15.438395 grains.
Gram = 0.03527 ounces avoirdupois.
Gram = 0.03216 ounces troy.
Kilogram = 2.205486 pounds avoirdupois.
Kilogram = 2.6803 pounds troy.

AVOIRDUPOIS.

Long ton = 2240 pounds = 1015.649 kilograms.
Short ton = 2000 pounds = 906.8296 kilograms.
Pound = 16 ounces = 7000 grains = 453.4148 grams.
Ounce = 437.5 grains = 28.3375 grams.
Grain = 64.773 milligrams = 0.064773 grams.

TROY.

Pound = 12 ounces = 5760 grains = 373.096 grams.
Ounce = 20 pennyweights = 480 grains = 31.0913 grams.
Pennyweight = 24 grains = 1.55457 grams.
Grain = 64.773 milligrams = 0.064773 grams.

TROY (Pharmacy.)

Ounce = 8 drams = 480 grains = 31.0913 grams.
Dram = 3 scruples = 60 grains = 3.8869 grams.
Scruple = 20 grains = 1.29546 grams.

TABLES OF MEASURES.

LENGTH.

Millimeter = 0.03937 inch.
Centimeter = 0.393708 inch.
Decimeter = 3.93708 inches.
Meter = 39.3708 inches.
Meter = 3.2809 feet.
Meter = 1.093633 yards.
Inch = 2.539954 centimeters.
Foot = 12 inches = 3.047945 decimeters.
Yard = 3 feet = 0.914383 meter.
Mile = 1760 yards = 5280 feet.
Mile = 1.609315 kilometers = 1609.315 meters.

SURFACE.

Square millimeter = 0.00155 square inches.
" centimeter = 0.155086 " "
" decimeter = 15.5086 " "
" decimeter = 0.10769 " foot.
" meter = 1550.86 " inches.
" meter = 10.7698 square feet = 1.196 " yards.

VOLUME.

Gallon U. S. = 231 cubic inches.
Gallon " = 3.78537 liters.
Quart " = 0.94634 liter.
Pint " = 0.47317 liter.
Liter = 2.1134 pints U. S. = 1.0567 quarts U. S. = 0.26417 gallon U. S.
Cubic meter = 1.308 cubic yards = 35.3171 cubic feet.
An imperial gallon, English = 277.274 cubic inches = 4.543458 liters.

ATOMIC WEIGHTS.

Reported by the Committee on Atomic Weights to the American Chemical Society.*

	H = 1	O = 16		H = 1	O = 16
Aluminium	26.91	27.11	Neodymium	142.52	143.60
Antimony	119.52	120.43	Nickel	58.24	58.69
Arsenic	74.44	75.01	Nitrogen	13.93	14.04
Barium	136.39	137.43	Osmium	189.55	190.99
Bismuth	206.54	208.11	Oxygen	15.88	16.00
Boron	10.86	10.95	Palladium	105.56	106.36
Bromine	79.34	79.95	Phosphorus	30.79	31.02
Cadmium	111.54	112.38	Platinum	193.41	194.89
Caesium	131.89	132.89	Potassium	38.82	39.11
Calcium	39.76	40.07	Praseodymium	139.41	140.46
Carbon	11.91	12.00	Rhodium	102.23	103.01
Cerium	138.30	139.35	Rubidium	84.78	85.43
Chlorine	35.18	35.45	Ruthenium	100.91	101.68
Chromium	51.74	52.14	Samarium	149.13	150.26
Cobalt	58.55	58.99	Scandium	43.78	44.12
Columbium	93.02	93.73	Selenium	78.58	79.17
Copper	63.12	63.60	Silicon	28.18	28.40
Erbium	165.06	166.32	Silver	107.11	107.92
Fluorine	18.91	19.06	Sodium	22.88	23.05
Gadolinium	155.57	156.76	Strontium	86.95	87.61
Gallium	69.38	69.91	Sulphur	31.83	32.07
Germanium	71.93	72.48	Tantalum	181.45	182.84
Glucinum	9.01	9.08	Tellurium	126.52	127.49
Gold	195.74	197.23	Terbium	158.80	160.00
Hydrogen	1.00	1.008	Thallium	202.61	204.15
Indium	112.99	113.85	Thorium	230.87	232.63
Iodine	125.89	126.85	Thulium	169.40	170.70
Iridium	191.66	193.12	Tin	118.15	119.05
Iron	55.60	56.02	Titanium	47.79	48.15
Lanthanum	137.59	138.64	Tungsten	183.43	184.83
Lead	205.36	206.92	Uranium	237.77	239.59
Lithium	6.97	7.03	Vanadium	50.99	51.38
Magnesium	24.10	24.28	Ytterbium	171.88	173.19
Manganese	54.57	54.99	Yttrium	88.35	89.02
Mercury	198.49	200.00	Zinc	64.91	65.41
Molybdenum	95.26	95.99	Zirconium	89.72	90.40

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* J. Am Chem. Soc. Feb. 1899.

TABLE OF FACTORS.

	Required.	Factor.	Logarithm.
Al_2O_3.	Al.	0.53042	$\bar{1}.72462$
$AlPO_4$.	Al.	0.22200	$\bar{1}.34631$
	Al_2O_3.	0.41849	$\bar{1}.62168$
Sb_2O_4.	Sb.	0.79010	$\bar{1}$ 89766
Sb_2S_3.	Sb.	0.71457	$\bar{1}.85404$
As_2S_3.	As.	0.60922	$\bar{1}.78477$
$Mg_2As_2O_7$.	As.	0.48300	$\bar{1}.68395$
Ag_3AsO_4.	As.	0.16209	$\bar{1}.20976$
$BaSO_4$.	BaO.	0.65709	$\bar{1}.81762$
	SO_3.	0.34291	$\bar{1}.53518$
	S.	0.13734	$\bar{1}.13781$
Bi_2O_3.	Bi.	0.89660	$\bar{1}.95260$
CdS.	Cd.	0.77798	$\bar{1}.89097$
$CaCO_3$.	CO_2.	0.43969	$\bar{1}.64315$
	CaO.	0.56037	$\bar{1}.74847$
CaF_2.	F.	0.48753	$\bar{1}.68800$
$CaSO_4$.	CaO.	0.41186	$\bar{1}.61475$
	$CaCO_3$.	0.73505	$\bar{1}.86632$
CO_2.	C.	0.27272	$\bar{1}.43572$
Cr_2O_3.	Cr.	0.68479	$\bar{1}.83556$
$3K_2SO_4, 2CoSO_4$.	Co.	0.14163	$\bar{1}.15115$
CuO.	Cu.	0.79900	$\bar{1}.90254$
Cu_2S.	Cu.	0.79864	$\bar{1}.90235$
Fe_2O_3.	Fe.	0.70008	$\bar{1}.84514$
Fe.	Fe_2O_3.	1.42842	0.15486
	FeO.	1.28561	0.10911
Fe.	Fe_3O_4.	1.38082	0.14014
$PbCrO_4$.	Pb.	0.64050	$\bar{1}.80652$
$PbSO_4$.	Pb.	0.68293	$\bar{1}.83437$
Li_3PO_4.	Li_2O.	0.38834	$\bar{1}.58921$
	LiCl.	1.09758	0.040436
$Mg_2P_2O_7$.	P.	0.27870	$\bar{1}.44514$
	P_2O_5.	0.63809	$\bar{1}.80488$
	MgO.	0.36190	$\bar{1}.55859$

TABLE OF FACTORS.

	Required.	Factor.	Logarithm.
	$MgCO_3$.	0.75722	$\bar{1}.87922$
Mn_3O_4.	Mn.	0.72049	$\bar{1}.85763$
$Mn_2P_2O_7$.	Mn.	0.38723	$\bar{1}.58796$
MnS.	Mn.	0.63163	$\bar{1}.80046$
$MnSO_4$.	Mn.	0.36403	$\bar{1}.56113$
HgS.	Hg.	0.86181	$\bar{1}.93541$
NiO.	Ni.	0.78578	$\bar{1}.89530$
$(NH_4)_2PtCl_6$.	Pt.	0.43920	$\bar{1}.64267$
	N	0.06328	$\bar{2}.80127$
	NH_3.	0.07691	$\bar{2}.88599$
	NH_4Cl.	0.24123	$\bar{1}.38244$
Pt from $(NH_4)_2PtCl_6$.	N.	0.14408	$\bar{1}.15861$
	NH_3.	0.17511	$\bar{1}.24332$
	NH_4Cl.	0.54925	$\bar{1}.73977$
K_2PtCl_6.	KCl.	0.30695	$\bar{1}.48707$
	K_2O.	0.19394	$\bar{1}.28768$
KCl.	K_2O.	0.63184	$\bar{1}.80061$
K_2SO_4.	K_2O.	0.54059	$\bar{1}.73287$
	K.	0.44872	$\bar{1}.65205$
SiO_2.	Si.	0.47020	$\bar{1}.67228$
AgBr.	Br.	0.42556	$\bar{1}.62896$
AgI.	I.	0.54031	$\bar{1}.73265$
AgCl.	Cl.	0.24726	$\bar{1}.39316$
	Ag.	0.75274	$\bar{1}.87664$
NaCl.	Na_2O.	0.53077	$\bar{1}.72491$
Na_2SO_4.	Na_2O.	0.43680	$\bar{1}.64028$
	Na.	0.32426	$\bar{1}.51089$
$SrSO_4$.	SrO.	0.56408	$\bar{1}.75134$
SnO_2.	Sn.	0.78815	$\bar{1}.89661$
TiO_2.	Ti.	0.60075	$\bar{1}.77869$
WO_3.	W.	0.79384	$\bar{1}.89973$
ZnO.	Zn.	0.80346	$\bar{1}.90497$
$Zn_2P_2O_7$.	Zn.	0.42911	$\bar{1}.63257$
$ZnNH_4PO_4$.	Zn.	0.36644	$\bar{1}.56400$

In most cases the factor to four places is sufficient.

SPECIFIC HEATS.

Lithium,	0.941	Copper,	0.0950
Carbon,	0.463	Zinc,	0.0935
Sodium,	0.273	Arsenic,	0.0830
Magnesium,	0.245	Molybdenum,	0.0659
Aluminum,	0.225	Silver,	0.0570
Silicon,	0.203	Cadmium,	0.0567
Phosphorus,	0.202	Tin,	0.0559
Sulphur,	0.178	Antimony,	0.0523
Potassium,	0.166	Tungsten,	0.0350
Calcium,	0.169	Mercury,	0.0328
Titanium,	0.148	Platinum,	0.0324
Manganese,	0.122	Gold,	0.0324
Iron,	0.112	Iridium,	0.0323
Nickel,	0.108	Lead,	0.0307
Cobalt,	0.107	Bismuth,	0.0305
Chromium,	0.100	Uranium,	0.0276

Thermometers.

Three scales are now in general use. These are :

1. Centigrade—C. Water freezes at 0°, boils at 100°.
2. Fahrenheit—F. " " 32°, " 212°.
3. Réaumur—R. " " 0°, " 80°.

To Convert—F. to C.

$$\left.\begin{array}{rl} \text{F. to C.} & \dfrac{5(\text{F.}^\circ-32^\circ)}{9}=\text{C.}^\circ \\ \text{C. to F.} & \dfrac{9\text{C.}^\circ}{5}+32^\circ=\text{F.}^\circ \\ \text{R to F.} & \dfrac{9\text{R.}^\circ}{4}+32^\circ=\text{F.}^\circ \end{array}\right\}\text{Formulæ.}$$

COMPARISON OF CENTIGRADE AND FAHRENHEIT DEGREES.

C°	F°	C°	F°	C°	F°	C°	F°	C°	F°
—40	—40	22	71.6	48	118.4	74	165.2	100	212
—30	—22	23	73.4	49	120.2	75	167	150	302
—20	— 4	24	75.2	50	122	76	168.8	200	392
—10	14	25	77	51	123.8	77	170.6	250	482
0	32	26	78.8	52	125.6	78	172.4	300	572
1	33.8	27	80.6	53	127.4	79	174.2	400	752
2	35.6	28	82.4	54	129.2	80	176	500	932
3	37.4	29	84.2	55	131	81	177.8	600	1112
4	39.2	30	86	56	132.8	82	179.6	700	1292
5	41	31	87.8	57	134.6	83	181.4	800	1472
6	42.8	32	89.6	58	136.4	84	183.2	900	1652
7	44.6	33	91.4	59	138.2	85	185	1000	1832
8	46.4	34	93.2	60	140	86	186.8	1100	2012
9	48.2	35	95	61	141.8	87	188.6	1200	2192
10	50	36	96.8	62	143.6	88	190.4	1300	2372
11	51.8	37	98.6	63	145.4	89	192.2	1400	2552
12	53.6	38	100.4	64	147.2	90	194	1500	2732
13	55.4	39	102.2	65	149	91	195.8	1600	2912
14	57.2	40	104	66	150.8	92	197.6	1700	3092
15	59	41	105.8	67	152.6	93	199.4	1800	3272
16	60.8	42	107.6	68	154.4	94	201.2	1900	3452
17	62.6	43	109.4	69	156.2	95	203	2000	3632
18	64.4	44	111.2	70	158	96	204.8	2500	4532
19	66.2	45	113	71	159.8	97	206.6	3000	5432
20	68	46	114.8	72	161.6	98	208.4		
21	69.8	47	116.6	73	163.4	99	210.2		

TABLE OF VALUES OF NORMAL SOLUTIONS.

Name.	Formula.	Molecular Weight.	Weight in Grams Per Liter.	Value in Grams of 1. C. C.
Sodium Oxide	Na_2O	62.1	31.05	0.03105
Sodium Hydroxide	$NaOH$	40.06	40.06	0.04006
Sodium Carbonate	Na_2CO_3	106.10	53.05	0 05305
Sodium Bicarbonate	$NaHCO_3$	84.06	84.06	0.08406
Potassium Oxide	K_2O	94.22	47.11	0.04711
Potassium Hydroxide	KOH	56.12	56.12	0.05612
Potassium Carbonate	K_2CO_3	138.22	69.11	0.06911
Potassium Bicarbonate	$KHCO_3$	100.12	100.12	0.10012
Ammonia	NH_3	17.06	17.06	0.01706
Ammonium Chloride	NH_4Cl	53.52	53.52	0.05352
Calcium Oxide	CaO	56.07	28.035	0.028035
Calcium Carbonate	$CaCO_3$	100.07	50.035	0.050035
Calcium Sulphate	$CaSO_4$	136.14	68.07	0.06807
Barium Hydroxide	$Ba(OH)_2$	171.45	85.725	0.085725
Barium Carbonate	$BaCO_3$	197.44	98.72	0.09872
Barium Chloride	$BaCl_2$	208.33	104.165	0.104165
Magnesium Oxide	MgO	40.28	20.14	0.02014
Sodium Sulphate	Na_2SO_4	142.17	71.085	0.071085
Potassium Sulphate	K_2SO_4	174.29	87.145	0.087145
Sulphuric Acid	H_2SO_4	98.09	49.045	0.049045
Nitric Acid	HNO_3	63.05	63.05	0.06305
Hydrochloric Acid.	HCl	36.46	36.46	0 03646
Oxalic Acid	$H_2C_2O_4$	90.02	45.01	0.04501

This and the following table are based on Oxygen 16. and the atomic weights given on page 159.

VALUES OF TENTH NORMAL SOLUTIONS.

Name	Formula.	Atomic or Molecular Weight.	Weight in Grams per Liter.	Value in Grms. of One C.C.
Potassium Permanganate....	$KMnO_4$	158.1	3.162	0.003162
Iron	Fe.	56.02	5.602	0.005602
Ferric Oxide...............	Fe_2O_3	160.04	8.002	0.008002
Ferrous Oxide..............	FeO	72.02	7.202	0.007202
Magnetic Oxide............	Fe_3O_4	232.06	7.735	0.007735
Ferrous Sulphate (Cryst)....	$FeSO_4.\ 7H_2O$	278.20	27.820	0.027820
Ferrous Ammonium Sulphate	$FeSO_4.\ (NH_4)_2SO_4.\ 6H_2O$	392.40	39.24	0.039240
Oxalic Acid (Cryst).........	$H_2C_2O_4.\ 2H_2O$	126.05	6.3025	0.0063025
Ammonium Oxalate (Cryst)..	$(NH_4)_2C_2O_4,\ H_2O$	142.16	7.108	0.007108
Calcium Oxide.............	CaO	56.07	2.8035	0.0028035
Calcium Carbonate..........	$CaCO_3$	100.07	5.0035	0.0050035
Calcium Sulphate (Cryst)....	$CaSO_4.\ 2H_2O$	172.17	8.6085	0.0086085
Manganese (Volhard)........	Mn.	54.99	1.65	0.00165
Manganese (Ford-Williams)..	Mn.	54.99	2.75	0.00275
Phosphorus (Noyes)........	P.	31.02	0.08616	0.00008616
Phosphoric Oxide (Noyes)...	P_2O_5	142.04	0.1973	0.0001973
Tin from $SnCl_2$	Sn	119.05	5.9525	0.0059525
Hydrogen Sulphide.........	H_2S	34.09	1.7043	0.0017043
Hydrogen Peroxide.........	H_2O_2	34.02	1.701	0.001701
Iodine	I	126.85	12.685	0.012685
Copper.....................	Cu	63.6	6.36	0.00636
Antimony	Sb	120.43	6.021	0.006021
Sulphurous Acid.,..........	H_2SO_3	82.09	4.1045	0.004104
Sulphur Dioxide............	SO_2	64.07	3.2035	0.003203
Sodium Thiosulphate........	$Na_2S_2O_3$	158.24	15.824	0.015824
Sodium Thiosulphate (Cryst).	$Na_2S_2O_3,\ 5H_2O$	248.32	24.832	0.024832
Chromium.................	Cr	52.14	1.738	0.001738
Chromic Oxide	Cr_2O_3	152.28	2.538	0.002538
Potassium Dichromate.......	$K_2Cr_2O_7$	294.5	4.9083	0.004908
Chlorine..................	Cl	35.45	3.545	0.003545
Potassium Chloride.........	KCl	74.56	7.456	0.007456
Sodium Chloride............	$NaCl$	58.5	5.85	0.00585
Ammonium Chloride........	NH_4Cl	53.52	5.352	0.00535
Silver....	Ag	107.92	10.792	0.01079
Silver Nitrate..............	$AgNO_3$	169.96	16.996	0.0170

Table of Comparison—Degrees of the Baumé Hydrometer and Specific Gravity.*

TABLE FOR LIQUIDS HEAVIER THAN WATER.

Degrees Baumé.	Specific Gravity.	Degrees Baumé	Specific Gravity.	Degrees Baumé.	Specific Gravity.
0	1.000	26	1.206	52	1.520
1	1.007	27	1.216	53	1.535
2	1.013	28	1.226	54	1.551
3	1.020	29	1.236	55	1.567
4	1.027	30	1.246	56	1.583
5	1.034	31	1.256	57	1.600
6	1.041	32	1.267	58	1.617
7	1.048	33	1.277	59	1.634
8	1.056	34	1.288	60	1.652
9	1.063	35	1.299	61	1.670
10	1.070	36	1.310	62	1.689
11	1.078	37	1.322	63	1.708
12	1.086	38	1.333	64	1.727
13	1.094	39	1.345	65	1.747
14	1.101	40	1.357	66	1.767
15	1.109	41	1.369	67	1.788
16	1.118	42	1.382	68	1.809
17	1.126	43	1.395	69	1.831
18	1.134	44	1.407	70	1.854
19	1.143	45	1.421	71	1.877
20	1.152	46	1.434	72	1.900
21	1.160	47	1.448	73	1.924
22	1.169	48	1.462	74	1.949
23	1.178	49	1.476	75	1.974
24	1.188	50	1.490	76	2.000
25	1.197	51	1.505		

TABLE FOR LIQUIDS LIGHTER THAN WATER.

Degrees Baumé.	Specific Gravity.	Degrees Baumé.	Specific Gravity.	Degrees Baumé.	Specific Gravity.
10	1.000	27	.896	44	.811
11	.993	28	.890	45	.807
12	.986	29	.885	46	.802
13	.980	30	.880	47	.798
14	.973	31	.874	48	.794
15	.967	32	.869	49	.789
16	.960	33	.864	50	.785
17	.954	34	.859	51	.781
18	.948	35	.854	52	.777
19	.942	36	.849	53	.773
20	.936	37	.844	54	.768
21	.930	38	.839	55	.764
22	.924	39	.834	56	.760
23	.918	40	.830	57	.757
24	.913	41	.825	58	.753
25	.907	42	.820	59	.749
26	.901	43	.816	60	.745

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* Crooke's Select Methods, p. 693.

VOLUME AND WEIGHT OF WATER FROM 0°C TO 31°C.*

Temperature.	Volume of one gram in c.c.	Weight of one c.c. in grams.	Temperature.	Volume of one gram in c.c.	Weight of one c c in grams.
0°	1.000126	0.999874	16°	1.001025	0.998976
1	1.000070	0.999930	17	1.001193	0.998808
2	1.000030	0.999970	18	1.001373	0.998629
3	1.000007	0.999993	19	1.001564	0.998438
4	1.000000	1.000000	20	1.001768	0.998235
5	1.000008	0.999992	21	1.001981	0.998023
6	1.000031	0.999969	22	1.002204	0.997801
7	1.000069	0.999931	23	1.002438	0.997568
8	1.000122	0.999878	24	1.002681	0.997326
9	1.000188	0.999812	25	1.002935	0.997073
10	1.000269	0.999731	26	1.003199	0.996811
11	1.000363	0.999637	27	1.003472	0.996540
12	1.000470	0.999530	28	1.003788	0.996226
13	1.000590	0.999410	29	1.004045	0.995971
14	1.000722	0.999278	30	1.004346	0.995673
15	1.000867	0.999134	31	1.004656	0.995365

For the most recent results on the expansion of water, which do not differ materially from the preceding, see Annalen d. Physik u. Chemie [N. F.] 60, 340, 1897.

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* Wied. Ann. 47.400. 1892.

Theoretical Densities of Gases Referred to Air and Weights of One Liter in Grams at 0°C and 760 m. m. Pressure.

Name.	Formula.	Density.	Weight of One Liter.*
Acetylene, ...	C_2H_2	0.89820	1.16143
Allylene, ...	C_3H_4	1.38194	1.78692
Ammonia, ...	NH_3	0.58890	0.76148
Arsine, ...	AsH_3	2.69728	3.48772
Bromine, ...	Br_2	5.52271	7.14115
Carbon Dioxide, . .	CO_2	1.51968	1.96503
Carbon Monoxide, . .	CO	0.96709	1.25050
Carbon Oxysulphide, .	COS	2.07483	2.68287
Chlorine, ...	Cl_2	2.44921	3.16696
Cyanogen, ...	$(CN)_2$	1.79907	2.32630
Ethane, ...	C_2H_6	1.03667	1.34047
Ethylene, ...	C_2H_4	0.96744	1.25095
Hydriodic Acid, . .	HI	4.41570	5.70972
Hydrobromic Acid, .	HBr	2.79597	3.61534
Hydrochloric Acid, .	HCl	1.25922	1.62824
Hydrofluoric Acid, .	HF	0.69178	0.89451
Hydrogen, ...	H_2	0.069234	0.089523
Hydrogen Sulphide, .	H_2S	1.17697	1.52189
Methane, ...	CH_4	0.55297	0.71502
Nitric Oxide, . . .	NO.	1.03764	1.34172
Nitrogen, ...	N_2	0.97010	1.25440
Nitrous Oxide, . . .	N_2O	1.52269	1.96892
Oxygen, ...	O_2	1.10521	1.42908
Phosphine, ...	PH_3	1.17552	1.52001
Silicon Tetrafluoride, .	SiF_4	3.60469	4.66105
Sulphur Dioxide, . .	SO_2	2.21295	2.86146
Water Vapor, . . .	H_2O	0.62182	0.80405
Air, ...		1.00000	1.29305

Taken from Hempel's Gas Analysis, Dennis.

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* These numbers are also the weight of a cubic meter in Kilograms.

VAPOR PRESSURE OF WATER FROM 0° C TO 100° C IN MILLIMETERS OF MERCURY.*

Temp.	Pressure.	Temp.	Pressure.	Temp.	Pressure.	Temp.	Pressure.
0	4.569	25	23.517	50	91.98	75	288.76
1	4.909	26	24.956	51	96.66	76	301.09
2	5.272	27	26.471	52	101.55	77	313.85
3	5.658	28	28.065	53	106.65	78	327.05
4	6.069	29	29.744	54	111.97	79	340.73
5	6.507	30	31.51	55	117.52	80	354.87
6	6.972	31	33.37	56	123.29	81	369.51
7	7.466	32	35.32	57	129.31	82	384.64
8	7.991	33	37.37	58	135.58	83	400.29
9	8.548	34	39.52	59	142.10	84	416.47
10	9.140	35	41.78	60	148.88	85	433.19
11	9.767	36	44.16	61	155.95	86	450.47
12	10.432	37	46.65	62	163.29	87	468.32
13	11.137	38	49.26	63	170.02	88	486.76
14	11.884	39	52.00	64	178.86	89	505.81
15	12.674	40	54 87	65	187.10	90	525.47
16	13.510	41	57 87	66	195.67	91	545.77
17	14.395	42	61.02	67	204.56	92	566.71
18	15.330	43	64.31	68	213.79	93	588.83
19	16.319	44	67.76	69	223.37	94	610.64
20	17.363	45	71.36	70	233.31	95	633.66
21	18.466	46	75.13	71	243.62	96	657.40
22	19.630	47	79.07	72	254.30	97	681.88
23	20.858	48	83.19	73	265.38	98	707.13
24	22.152	49	87 49	74	276.87	99	733.16

* Taken from Ostwald's Manual of Physico-Chemical Measurements.

TABLE OF SPECIFIC GRAVITY AND PERCENTAGE OF ALCOHOL (ETHYL).*

Per Cent. by Volume.	Per Cent. by Weight.	Specific Gravity at 15.56°C.	Per Cent. by Volume.	Per Cent by Weight.	Specific Gravity at 15.56°C.
0	0.00	1.0000	51	43.47	.9315
1	0.80	.9976	52	44.42	.9295
2	1.60	.9961	53	45.36	.9275
3	2.40	.9947	54	46.32	.9254
4	3.20	.9933	55	47.29	.9234
5	4.00	.9919	56	48.26	.9213
6	4.81	.9906	57	49.23	.9192
7	5.62	.9893	58	50.21	.9170
8	6.43	.9881	59	51.20	.9148
9	7.24	.9869	60	52.20	.9126
10	8.05	.9857	61	53.20	.9104
11	8.87	.9845	62	54.21	.9082
12	9.69	.9834	63	55.21	.9059
13	10.51	.9823	64	56.22	.9036
14	11.33	.9812	65	57.24	.9013
15	12.15	.9802	66	58.27	.8989
16	12.98	.9791	67	59.32	.8965
17	13.80	.9781	68	60.38	.8941
18	14.63	.9771	69	61.42	.8917
19	15.46	.9761	70	62.50	.8892
20	16.28	.9751	71	63.58	.8867
21	17.11	.9741	72	64.66	.8842
22	17.95	.9731	73	65.74	.8817
23	18.78	.9720	74	66.83	.8791
24	19.62	.9710	75	67.93	.8765
25	20.46	.9700	76	69.05	.8739
26	21.30	.9689	77	70.18	.8712
27	22.14	.9679	78	71.31	.8685
28	22.99	.9668	79	72.45	.8658
29	23.84	.9657	80	73.59	.8631
30	24.69	.9646	81	74.74	.8603
31	25.55	.9634	82	75.91	.8575
32	26.41	.9622	83	77.09	.8547
33	27.27	.9609	84	78.29	.8518
34	28.13	.9596	85	79.50	.8488
35	28.99	.9583	86	80.71	.8458
36	29.86	.9570	87	81.94	.8428
37	30.74	.9556	88	83.19	.8397
38	31.62	.9541	89	84.46	.8365
39	32.50	.9526	90	85.75	.8332
40	33.39	.9510	91	87.09	.8299
41	34.28	.9494	92	88.37	.8265
42	35.18	.9478	93	89.71	.8230
43	36.08	.9461	94	91.07	.8194
44	36.99	.9444	95	92.46	.8157
45	37.90	.9427	96	93.89	.8118
46	38.82	.9409	97	95.34	.8077
47	39.75	.9391	98	96.84	.8034
48	40.66	.9373	99	98.39	.7988
49	41.59	.9354	100	100.00	.7939
50	42.52	.9335			

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* Tralles.

PERCENTAGE AND SPECIFIC GRAVITY OF SULPHURIC ACID AT 15° C.* WATER AT 0° C. = 1.

Percent.	Sp. Gr.	Percent.	Sp. Gr.	Percent.	Sp. Gr.	Percent.	Sp. Gr.
1	1.006	26	1.191	51	1.409	76	1.684
2	1.012	27	1.199	52	1.418	77	1.697
3	1.018	28	1.207	53	1.428	78	1.710
4	1.025	29	1.215	54	1.438	79	1.721
5	1.032	30	1.223	55	1.448	80	1.732
6	1.039	31	1.231	56	1.459	81	1.743
7	1.046	32	1.239	57	1.469	82	1.753
8	1.053	33	1.247	58	1.480	83	1.763
9	1.061	34	1.256	59	1.491	84	1.773
10	1.069	35	1.264	60	1.501	85	1.783
11	1.076	36	1.272	61	1.512	86	1.792
12	1.084	37	1.281	62	1.523	87	1.800
13	1.091	38	1.290	63	1.535	88	1.807
14	1.099	39	1.298	64	1.546	89	1.814
15	1.106	40	1.307	65	1.558	90	1.820
16	1.114	41	1.316	66	1.569	91	1.825
17	1.122	42	1.324	67	1.580	92	1.8294
18	1.129	43	1.333	68	1.592	93	1.8339
19	1.137	44	1.342	69	1.604	94	1.8372
20	1.145	45	1.352	70	1.615	95	1.8390
21	1.153	46	1.361	71	1.626	96	1.8406
22	1.161	47	1.370	72	1.638	97	1.8410
23	1.168	48	1.379	73	1.650	98	1.8412
24	1.176	49	1.389	74	1.662	99	1.8403
25	1.184	50	1.399	75	1.674	100	1.8384

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* Gerlach Z. Anal. Chem. 27,316.

PERCENTAGE AND SPECIFIC GRAVITY OF NITRIC ACID AT 15°C. *

Per Cent.	Sp. Gr.	Per Cent.	Sp. Gr.	Per Cent.	Sp. Gr.	Per Cent.	Sp. Gr.
1	1.006	26	1.159	51	1.323	76	1.445
2	1.012	27	1.166	52	1.329	77	1.449
3	1.018	28	1.172	53	1.335	78	1.452
4	1.024	29	1.179	54	1.341	79	1.456
5	1.029	30	1.185	55	1.346	80	1.460
6	1.035	31	1.192	56	1.352	81	1.463
7	1.040	32	1.198	57	1.358	82	1.467
8	1.045	33	1.204	58	1.363	83	1.470
9	1.051	34	1.210	59	1.369	84	1.474
10	1.057	35	1.218	60	1.374	85	1.478
11	1.064	36	1.225	61	1.380	86	1.481
12	1.070	37	1.230	62	1.386	87	1.484
13	1.077	38	1.236	63	1.390	88	1.488
14	1.083	39	1.244	64	1.395	89	1.491
15	1.089	40	1.251	65	1.400	90	1.495
16	1.095	41	1.257	66	1.405	91	1.499
17	1.100	42	1.264	67	1.410	92	1.503
18	1.106	43	1.270	68	1.414	93	1.506
19	1.112	44	1.276	69	1.419	94	1.509
20	1.120	45	1.284	70	1.423	95	1.512
21	1.126	46	1.290	71	1.427	96	1.516
22	1.132	47	1.298	72	1.431	97	1.520
23	1.138	48	1.304	73	1.435	98	1.523
24	1.145	49	1.312	74	1.439	99	1.526
25	1.151	50	1.316	75	1.442	100	1.530

* Kolb, Gerlach, Z. Anal. Chem. 8,292.

SPECIFIC GRAVITY AND PERCENTAGE OF HYDROCHLORIC ACID AT 15° C.* WATER AT 4° C. = 1.

Sp. Gr.	% HCl.	Sp. Gr.	% HCl.
1.000	0.16	1.105	20.97
1.005	1.15	1.110	21.92
1.010	2.14	1.115	22.86
1.015	3.12	1.120	23.82
1.020	4.13	1.125	24.78
1.025	5.15	1.130	25.75
1.030	6.15	1.135	26.70
1.035	7.15	1.140	27.66
1.040	8.16	1.145	28.61
1.045	9.16	1.150	29.57
1.050	10.17	1.155	30.55
1.055	11.18	1.160	31.52
1.060	12.19	1.165	32.49
1.065	13.19	1.170	33.46
1.070	14.17	1.175	34.42
1.075	15.16	1.180	35.39
1.080	16.15	1.185	36.31
1.085	17.13	1.190	37.23
1.090	18.11	1.195	38.16
1.095	19.06	1.200	39.11
1.100	20.01		

For other similar tables see Comey's Dictionary of Chemical Solubilities.

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* Lunge and Marchlewski Zeit. f. angew. Chem. 1891. 133.

SPECIFIC GRAVITY AND PERCENTAGE OF AMMONIA* AT 15° C.

Sp. Gr.	% NH_3	Sp. Gr.	% NH_3	Sp. Gr.	% NH_3
1.000	0.00	0.960	9.91	0.920	21.75
0.998	0.45	0.958	10.47	0.918	22.39
0.996	0.91	0.956	11.03	0.916	23.03
0.994	1.37	0.954	11.60	0.914	23.68
0.992	1.84	0.952	12.17	0.912	24.33
0.990	2.31	0.950	12.74	0.910	24.99
0.988	2.80	0.948	13.31	0.908	25.65
0.986	3 30	0.946	13.88	0.906	26.31
0.984	3.80	0.944	14.46	0.904	26.98
0.982	4.30	0.942	15.04	0.902	27.65
0.980	4.80	0.940	15.63	0.900	28.33
0.978	5.30	0.938	16.22	0 898	29.01
0.976	5.80	0.936	16.82	0.896	29.69
0.974	6.30	0.934	17.42	0.894	30.37
0.972	6.80	0.932	18.03	0.892	31.05
0.970	7.31	0.930	18.64	0.890	31.75
0.968	7.82	0.928	19.25	0.888	32.50
0.966	8.33	0.926	19.87	0.886	33.25
0.964	8.84	0.924	20.49	0.884	34.10
0.962	9.35	0.922	21.12	0.882	34.95

* Lunge and Wiernik Zeit. f. angew. Chem. 1889. 183.

TABLE SHOWING THE RELATIONS BETWEEN UNITS OF ELECTRICITY, HEAT AND POWER.

1 ampere = 1 volt ÷ 1 ohm.
= 1 coulomb per second.
1 ampere hour = 1 coulomb per second kept up for one hour.
1 ampere hour = 3600 coulombs.
1 volt = 1 ampere × 1 ohm.
1 ohm = 1 volt ÷ 1 ampere.
1 joule = 1 volt × 1 coulomb.
" = .2381 calorie.
" = .73732 foot-pound.
" = .10194 kilogram-meter.
1 calorie = 4.2 joules.
" = 3.0968 foot-pounds.
" = .42815 kilogram-meter.
1 foot pound = 1.3563 joules.
" = .32292 calorie.
" = .13825 kilogram-meter
1 kilogram meter = 9.81 joules.
" = 2.3362 calories.
" = 7.233 foot-pounds.
1 watt-hour = 1 watt kept up for one hour.
1 watt-hour = 1 joule per second kept up for one hour.
1 watt-hour = 3600 joules.
" = 857.16 calories.
" = 2654.4 foot-pounds.
" = 366.98 kilogram-meters
1 watt = 1 joule per second.
" = .2381 calorie per second.
" = .73732 foot-pound per second.
1 watt = .10194 kilogram-meter per second.
1 watt = .0013406 horse-power.
" = .001 kilowatt.
1 horse-power = 745.94 watts.
" = 177.6 calories per second.
1 horse-power = 10656. calories per minute.
1 horse-power = 550 foot pounds per second.
1 horse-power = 33000 foot pounds per minute.
1 horse-power = 76.04 kilogram-meters per second.
1 horse-power = 4562.4 kilogram-meters per minute.
1 horse-power = .74594 kilowatts.
1 kilowatt = 1000 watts.
" = 1000 joules per second.
" = 238.1 calories per second.
" = 14286. calories per minute
" = 737.32 foot-pounds per second.
1 kilowatt = 44239. foot-pounds per minute.
1 kilowatt = 101.94 kilogram-meters per second.
1 kilowatt = 6116.4 kilogram-meters per minute.
1 kilowatt = 1.3406 horse-power.

Table of Electro-Chemical Equivalents based on the definition of the ampere and the atomic weights, oxygen being 16, as given on page 159.

Element.	Atomic Weight.	Valency.	Chemical Equivalent.	Electro-chemical Equivalent. Grams per coulomb.)	Coulombs per gram.	Grams per ampere-hour.	Ampere-hour-per pound.
Electropositive.							
Aluminium	27.11	3.	9.037	.00009362	10680.	.3370	1346.
Antimony	120.43	3.	40.14	.0004159	2405.	1.497	303 0
Bismuth	208.11	3.	69.37	.0007186	1392.	2 587	175.3
Cadmium	112.38	2.	56.19	.0005821	1718.	2.096	216.4
Cobalt	58.99	2.	29.5	.0003056	3272.	1.100	412.2
Copper (Cuprous)	63.6	1.	63.6	.0006589	1518.	2.372	191.2
Copper (Cupric)	63.6	2.	31.8	.0003295	3036.	1.186	382.4
Gold	197.23	3.	65.78	.0006815	1467.	2.453	184.7
Hydrogen	1.008	1.	1.008	.00001044	95785.	.03758	12070.
Iron (Ferrous)	56.02	2.	28.01	.0002902	3446.	1.045	434.0
Iron (Ferric)	56.02	3.	18.67	.0001934	5171.	.6962	651.5
Lead	206.92	2.	103.5	.001072	932.8	3.859	117.5
Magnesium	24.28	2.	12.14	.0001258	7949.	.4528	1001.
Manganese	54.99	2.	27.50	.0002849	3510.	1.026	442.1
Mercury (Mercurous)	200.	1.	200.	.002072	482.6	7.459	60.81
Mercury (Mercuric)	200.	2.	100.	.001036	965.3	3.730	121.6
Nickel	58.69	2,	29.35	.0003041	3288.	1.095	414.2
Platinum	194.89	4.	48.72	.0005047	1981.	1.817	249.6
Potassium	39.11	1.	39.11	.0004052	2468.	1.459	310.9
Silver	107 92	1.	107.92	.001118	894.5	4.025	112.7
Sodium	23.05	1.	23.05	.0002388	4188.	.8597	527.6
Tin (Stannous)	119.05	2.	59.52	.0006166	1622.	2.220	204.3
Tin (Stannic)	119.05	4.	29.76	.0003083	3243.	1.110	408.6
Zinc	65.41	2.	32.70	.0003388	2952.	1.220	371.8
Electronegative.							
Bromine	79.95	1.	79.95	.0008283	1207.	2.982	152.1
Chlorine	35.45	1.	35.45	.0003673	2723.	1.322	343.1
Iodine	126.85	1.	126.85	.001314	761.0	4.730	95.90
Nitrogen	14.04	3.	4.68	.00004848	20627.	.1745	2599.
Oxygen	16.	2.	8.	.00008288	12066.	.2984	1520.

Heats of Combination in Calories, for Equivalent Weights in grams, of Chlorides, Bromides, Iodides, Sulphates and Nitrates.*

Element.	Valence.	Chloride.	Bromide.	Iodide.	Sulphate.	Nitrate.
Aluminium	3	53660	39900	23463	25315	
Antimony	3	30463				
Bismuth	3	30210				
Cadmium	2	46620	37600	24215	44940	43000
Cobalt	2	38240			44350	42270
Copper	1	32875	24985	16260		
Copper	2				27980	26205
Gold	3	7607	2950			
Hydrogen	1	39315	28380	13170	39170	33830
Iron	2	41025			46600	44835
Lead	2	41385	32225	19900		34035
Magnesium	2	75505			90090	88240
Manganese	2	55995			60625	58860
Mercury	2	31580	17155			18535
Nickel	2	37265			43475	41710
Silver	1	29380	22700	13800	10195	8390
Tin	2	40395				
Zinc	2	48605	37965	24615	53045	51255

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* These values are taken from Thomsen's Thermo-chemische Untersuchungen. The sulphates, nitrates and hydrogen compounds are for aqueous solutions. The chlorides, bromides and iodides are anhydrous.

SPECIFIC RESISTANCE OF VARIOUS SUBSTANCES.

Substance.	Temperature.	Specific Gravity.	ρ in ohms.	% Solution.	Observer.
Silver (annealed)	0°C.	10.6	.000001500		Matthiesen.
Silver (hard drawn)	"	10.6	.000001530		"
Copper (annealed)	"	8.9	.000001594		"
Copper (hard drawn)	"	8.9	.000001629		"
Gold (annealed)	"	19.3	.000002052		"
Gold (hard drawn)	"	19.3	.000002089		"
Aluminium (annealed)	"	2.6	.000002903		"
Platinum (annealed)	"	21.2	.000009030		"
Iron (annealed)	"	8.1	.000009687		"
Tin (pressed)	"	7.3	.00001317		"
Zinc (pressed)	"	7.1	.000005598		"
Lead (pressed)	"	11.4	.00001957		"
Nickel (pressed)	"	8.5	.00001242		"
German Silver	"		about .0000209		"
Graphite	"	2.3	.0024 to .042		Everett.
Retort Carbon	"	1.9	.07		"
Mercury	"	13.6	.000094073 *		
Nitric Acid in water	18°C.	1.185	1.28 †	29.7	Kohlrausch.
Hydrochloric Acid in water	"	1.092	1.31 †	18.3	"
Sulphuric Acid in water	"	1.224	1.36 †	30.4	
Phosphoric Acid in water	"	1.307	4.79 †	46.8	"
Tartaric Acid in water	"	1.107	9.97 †	22.4	"
Acetic Acid in water	"	1.022	61.9 †	16.6	"
Ammonium Chloride in water	10°C.		2.5 †		Kohlrausch and Nippoldt.
Sodium Chloride in water	"		4.7 †		
Sodium Sulphate in water	"		11.3 †		
Zinc Sulphate in water	"	1.270	28.5 †		Ewing & Macgregor
Zinc Sulphate in water	"	1.422	33.7 ‡		" "
Copper Sulphate in water	"	1.205	29.3 ‡		" "
Potassium Sulphate in water	"		16.6 ‡		" "
Potassium Bichromate in water	"		29.6 ‡		" "

Further data on the conductivity of solutions can be found in Physikalisch-Chemische Tabellen, Landolt and Bornstein, pp. 103, 106.

Kohlrausch and Nippoldt, Pogg. Ann. 138 p. 379, 1869.

Grotrian " " 151 p. 378, 1874.

Kohlrausch and Grotrian, Pogg. Ann. 159 p. 233, 1876 and Wied. Ann. 6, p. 145, 1879.

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* From the definition of the ohm.

† Solution of minimum resistance.

‡ Saturated solution.

Comparison of Calculated and Observed Decomposition Voltages of various Aqueous Solutions.

	Chloride.		Bromide.		Iodide.		Sulphate.		Nitrate.	
	Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed.
Magnesium.	3.28	3.1		2.56		2.01	3.91		3.83	
Zinc. . . .	2.11	2.11	1.65	1.79	1.07	1.25	2.31	2.35	2.23	
Cadmium. .	2.03	1.9	1.63	1.58	1.06	1.12	1.95	2.03	1.87	1.98
Aluminium.	2.33	2.0	1.74	1.53	1.02	.88			1.10	
Iron. . . .	1.78	1.6		1.30		.68	2.03		1.95	
Cobalt. . .	1.66	1.43		1.05		.51	1.91	1.92	1.84	
Nickel. . . .	1.62	1.33		.85		.36	1.89	2.09	1.81	
Tin.	1.76	1.61		1.30		.71				
Lead. . . .	1.80	1.63	1.40	1.33	.87	.83			1.48	1.52
Copper. . .	1.43	1.32	1.09	1 02	.71	.64	1.22		1.14	
Silver. . .	1.28	1.11	.99	.95	.60	.65	.44		.365	.36*
Antimony. .	1.32	1.22		.80		.44				
Bismuth. .	1.31	1.21		.92		.43				
Hydrogen. .	1.71	1.31	1.23	.94	.57	.52	1.70	1.67	1.81	1.69

The observed decomposition values of the acids given under hydrogen together with many of the sulphates and nitrates are taken from LeBlanc's Electro Chemistry pp. 247-8. The other observed values are from Crocker, Trans. Am. Inst. E.E. 1885, p. 281.

The calculated values are obtained by substituting the heats of combination on page 177 in equation (14) $E = \frac{H}{23000}$.

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* Experiment.

Natural Numbers.	0	1	2	3	4	5	6	7	8	9	Proportional Parts.								
											1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7039	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7334	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

Natural Numbers.	0	1	2	3	4	5	6	7	8	9	Proportional Parts.								
											1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

ANTILOGARITHMS.

Logarithms.	0	1	2	3	4	5	6	7	8	9	Proportional Parts.								
											1	2	3	4	5	6	7	8	9
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6

Loga-rithms	0	1	2	3	4	5	6	7	8	9	Proportional Parts.								
											1	2	3	4	5	6	7	8	9
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
.59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
.65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
.72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
.76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
.79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
.82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
.84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
.85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
.87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
.93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
.99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20